Unconventional hydrogen and dihydrogen bonded supramolecular array of a 2,6-dioxa-9,16-diaza-1,3(1,2),4(1,4)-tribenzenacycloheptadecaphane-borane adduct

**Viviana Reyes-Márquez,[a] Karen Ochoa Lara,[a*] Mario Sánchez,[a]
and Juan Carlos Gálvez-Ruiz[b*]**

[a]*Departamento de Investigación en Polímeros y Materiales,*
[b]*Departamento de Ciencias Químico-Biológicas, Universidad de Sonora, Blvd. Luis Encinas y
Rosales, S/N, 83000, Apartado Postal 130, Hermosillo, Sonora, México*
E-mail: anisolborano@guayacan.uson.mx

Dedicated to Prof. Rosalinda Contreras on the occasion of her 60th birthday

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Abstract

The crystal structure of the title borane-oxaazacyclophane adduct consists of a tri-dimensional supramolecular array sustained by unconventional N-H···H-B and C-H···H-B dihydrogen bonding and weak C-H···π interactions. The interchain organization in the crystal structure is characterized by weak C-H···H-B dihydrogen bonds.

Keywords: Dihydrogen bond, unconventional bond, borane adduct, azacyclophane, supramolecular array

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Introduction

The importance of hydrogen bonds in many physical, chemical, and biological processes is broadly accepted nowadays. Typical hydrogen bonds are those where the hydrogen atom lies between two electronegative atoms, described as X-H···Y (X, Y = O, N, F). Hydrogen bonds that involve donors and/or acceptors different from those described previously are called unconventional hydrogen bonds. Different types of unconventional hydrogen bonds, such as those where the acceptors correspond to a π electron density, a metal-hydrogen bond and where the donors are C–H, have been described.[1] Experimental and theoretical studies have been performed to understand the nature of these unconventional hydrogen bonds,[1a-b, 2] because they play key roles to elucidate some physical, chemical, and biological properties.[3]

The dihydrogen bond,[1a-b] described as X-H···H-Y (X = O, N, Y = B or transition metal) is possibly the most surprising unconventional hydrogen bond due to its nature and ability to influence the structure, reactivity, and selectivity in both solution and solid state.[4]

Several structural and energetic similarities have been observed between the conventional hydrogen bond and the dihydrogen bond. The H···H distance in X–H···H–Y systems typically ranges from 1.7 to 2.4 Å. The interaction energy also lies within the range of typical hydrogen bonds, 3–10 kcal/mol. The linearity of normal hydrogen bonds is preserved in unconventional hydrogen bonds. The H···H–X angles generally lie within 160-180°. However, the Y–H···H angles are found to be strongly bent, falling in the range of 95– 130°.[2c]

The C-H···π interaction is another class of unconventional hydrogen bonds that is gaining attention because of its role as the driving force in determining crystal packing, molecular conformation, and alignment of liquid crystals.[5] This interaction is characterized by an inter- or intra-molecular distance in the range of 2.6-3.0 Å. Furthermore, the C-H bond points close to the center of an aromatic ring and the angle between the C-H bond and the center of the aromatic ring is close to linearity.[2d] Despite being the weakest hydrogen bond, the C-H···π interaction can influence the molecular recognition pattern in a host-guest system and should, therefore, be taken into account.[2b]
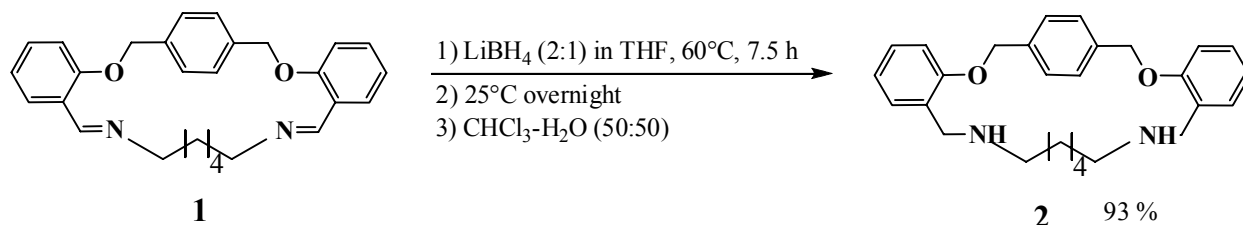
On the other hand, the H_3NBH_3 complex is perhaps the most studied complex with dihydrogen bonds. It exhibits multiple N-H···H-B intermolecular interactions in the solid state with H···H distance of 2.02 Å.[6] Besides, it has been proposed that some physical properties of this compound come from the dihydrogen bonds.[7]

Borane-amine adducts are widely used in modern synthetic organic chemistry because of their capability to carry out reductions of aldehydes and ketones, reductive aminations, olefin hydroborations, and amide reductions. Complexes of amine-boranes have also been utilized as chiral transfer agents, and as a protective device against nitrogen lone pair oxidation.[8] Usually, borane-amine complexes are readily formed by reduction of amides, imides, and imines, or by treatment of the corresponding amine with diborane or borane.

We are interested in the synthesis, characterization, and molecular recognition studies of synthetic and semi-synthetic macrocycles.[9] During the course of our research, in attempting to obtain one of these macrocyclic compounds, we obtained a borane adduct; hence, the aim of the present work is to emphasize the relevance of unconventional hydrogen bonds, such as proton-hydride and C-H···π, in organizing interactions in the borane-azacyclophane complex in the solid state.

Results and Discussion

In order to prepare macrocycle **2**, we reacted the Schiff base **1** with LiBH$_4$ in THF,[9b] Scheme 1.

Scheme 1. Reduction of Schiff base **1** to **2**.

The reaction was monitored by TLC (heptane:acetone, 60:40) until a single product was observed and the starting material disappeared. Then, water was added and generation of gas was observed. Purification by chloroform-water extraction produced a stable white powder with a very good yield.

As expected, the IR-spectrum of the product showed N-H stretching (3268 cm^{-1}), and the characteristic band for imine group (1644 cm^{-1}) was not observed. Besides, four unexpected bands were present at 2390, 2271, 1603, and 1590 cm^{-1}. First we thought that LiBH$_4$ was present but the ^{1}H NMR spectrum of this product was much more complex than that we had expected for the macrocycle **2**; we then concluded that this compound should be the borane-oxaazacyclophane **3** (see Figure 1) having its nitrogen atoms as chiral centers and therefore hydrogen atoms on the adjacent carbon are now diastereotopic. To confirm the assigned structure, the ^{11}B NMR spectrum was recorded and a broad signal (3764 Hz) at δ = -17 ppm was observed. The ^{11}B-^{1}H coupled spectrum gave an even broader signal (5621 Hz).
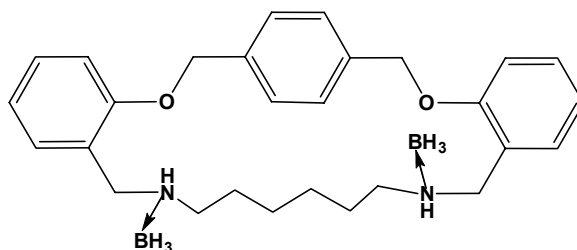

Figure 1. Borane-oxaazacyclophane adduct **3**.

It is important to point out that compound **3** is air- and hydrolysis-stable even in basic media. This increased stability may be attributed to some structural and electronic effects present in the molecule.

We were able to get single crystals of compound **3,** and the crystalline structure is shown in Figure 2. In this figure, the 17-membered oxaazacyclophane with two BH_3 groups, coordinated to its nitrogen atoms, can be seen. The internal ring cavity dimension is 8.53 x 5.14 Å.
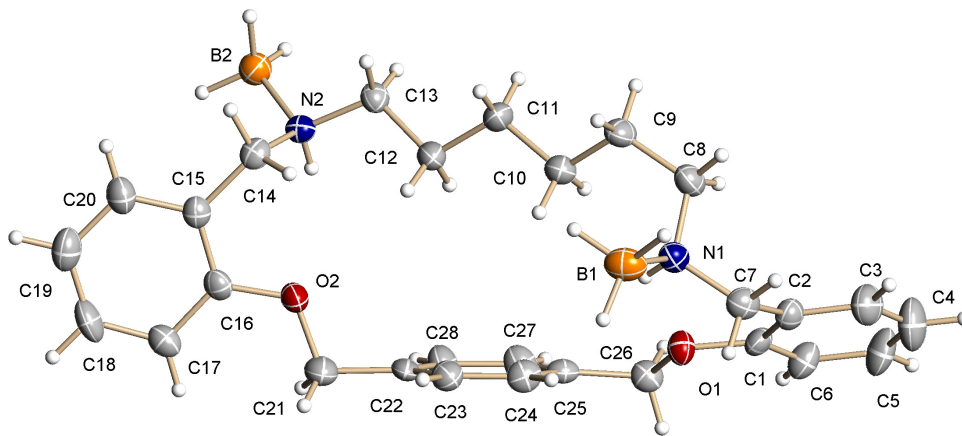

Figure 2. Crystalline structure of compound **3**.

The solid state structure of compound **3** presents very interesting structural features. First, one molecule of $CHCl_3$ has co-crystallized with compound **3** and it is located close to one BH_3 group, see Figure 3A. A short inter-molecular dihydrogen bond is observed with a C-H···H-B distance of 1.93 Å, which is shorter than the sum of the van der Waals radii for two hydrogen atoms (2.4 Å). The C-H···H and B-H···H angles are 147.1 and 114.5º, respectively. Second, an N-H···H-B dihydrogen bonding interaction is observed between the hydrogen atom of the NH fragment of the macrocycle and a coordinated BH_3 group of a symmetry-related molecule, resulting in the formation of a dimer linked by two short, 2.21 Å, dihydrogen bonds (see Figure 3B). The H···H-B angle was 118.3°, whereas the H···H-N angle was 158.9°. This type of linear N-H···H and bent B-H...H geometry is consistent with other examples of close $H^+···^-H$ contacts for crystallographically characterized amine-borane species.[6, 10]
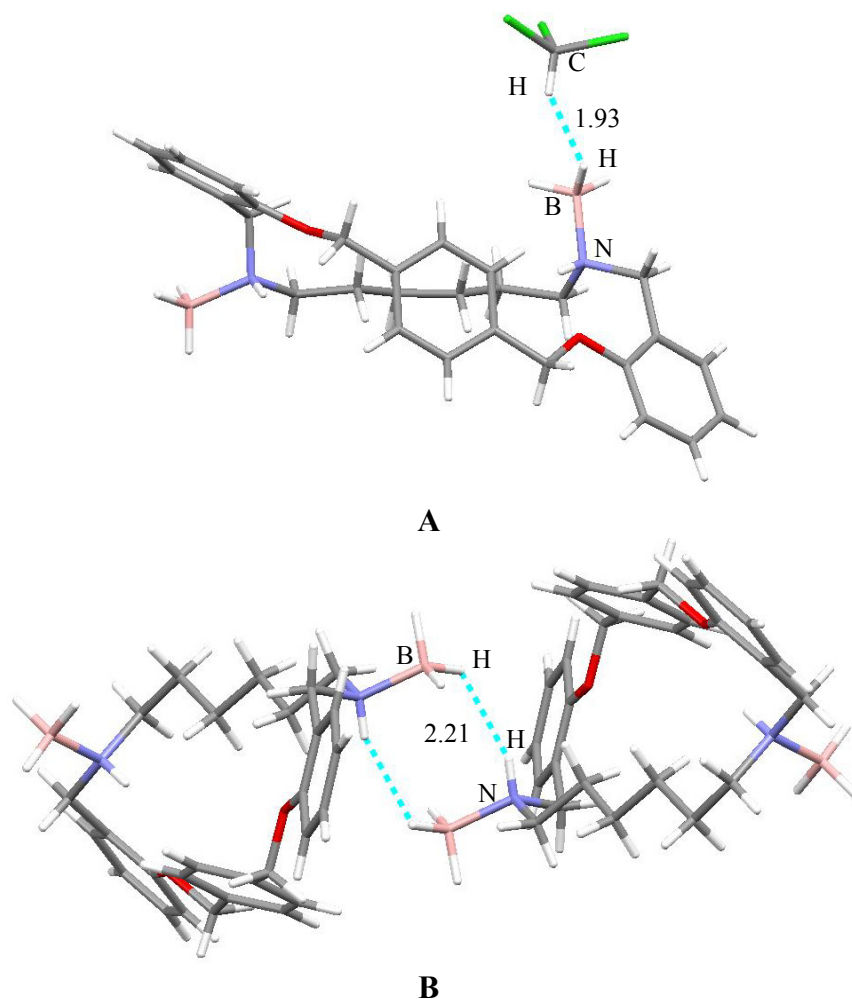
A

B

Figure 3. Intermolecular dihydrogen bonds in the lattice of **3**.

Third, one C-H bond of the nitrogen adjacent methylene group points close to the center of an aromatic ring, giving a C-H···π interaction, see Figure 4. The crystallographic distance C-H···center of the aromatic ring (centroid) and the angle C-H-centroid are 2.85 Å and 155º, respectively.   Both, the distance C-H···centroid (in the accepted range of 2.6-3.0 Å[2d]) and the angle close to linearity, confirm the C-H···π interaction.
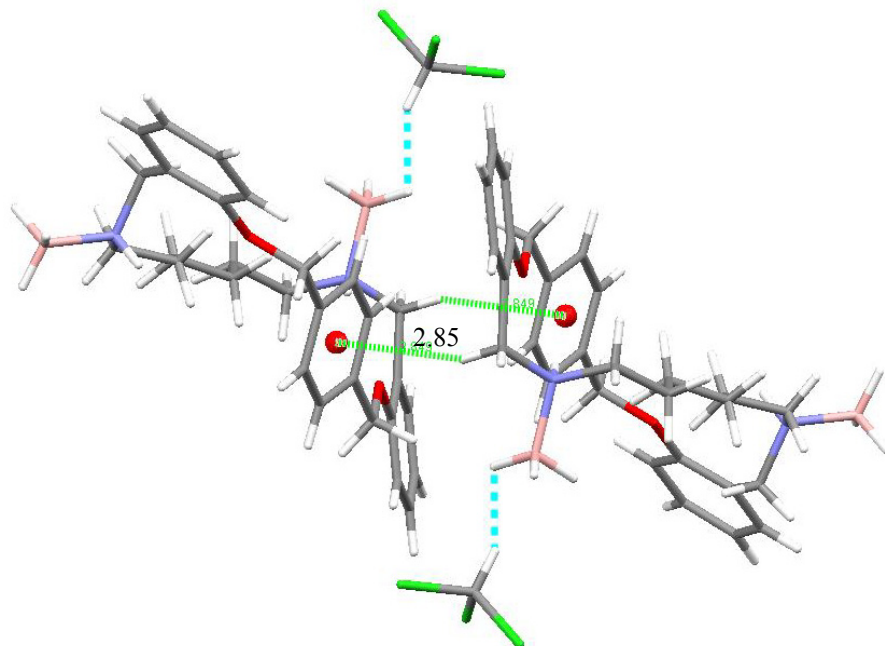
Figure 4. Intermolecular C-H···π interactions in the lattice of **3**.

All these unconventional hydrogen bonds correspond to the supramolecular array scaffolds observed in compound **3**. This array is shown in Figure 5, and consists of a chain of dimers kept together by N-H···H-B and C-H···π hydrogen bonds, being the N-H···H-B hydrogen bond the central part of the chain. In the lattice, the chains of dimers are linked by a very weak C-H···H-B dihydrogen bond (distance H^+···$^-$H, 2.5 Å; C-H···H angle, 140.5°; see Figure 6). It is interesting to note that only one of the BH_3's participates in the molecular array because the other one is only involved in a C-H···H-B hydrogen bond with the $CHCl_3$ molecule.
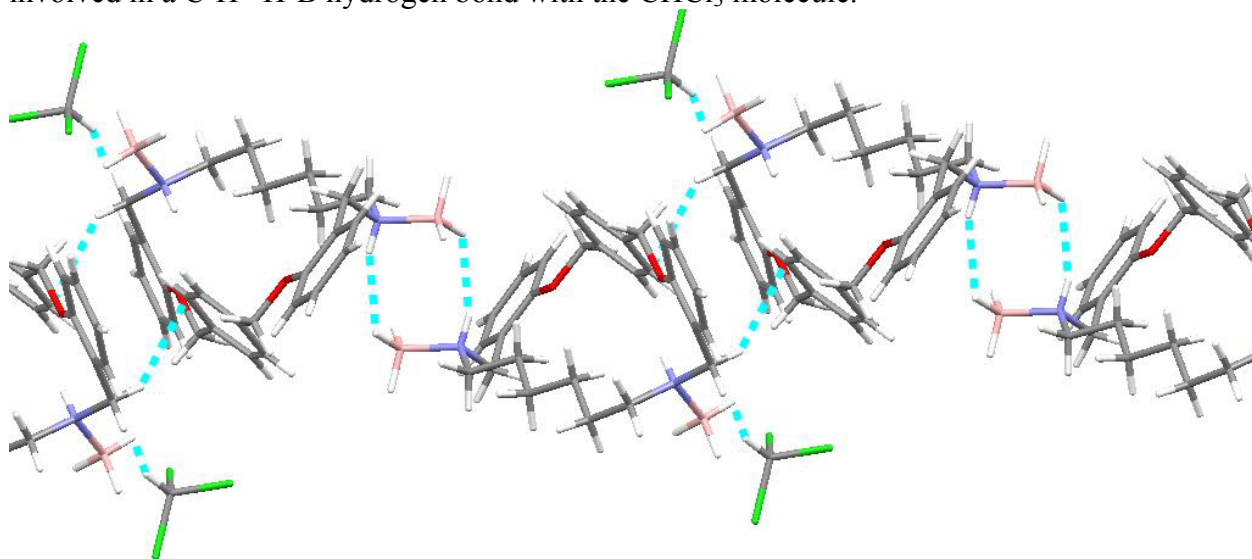

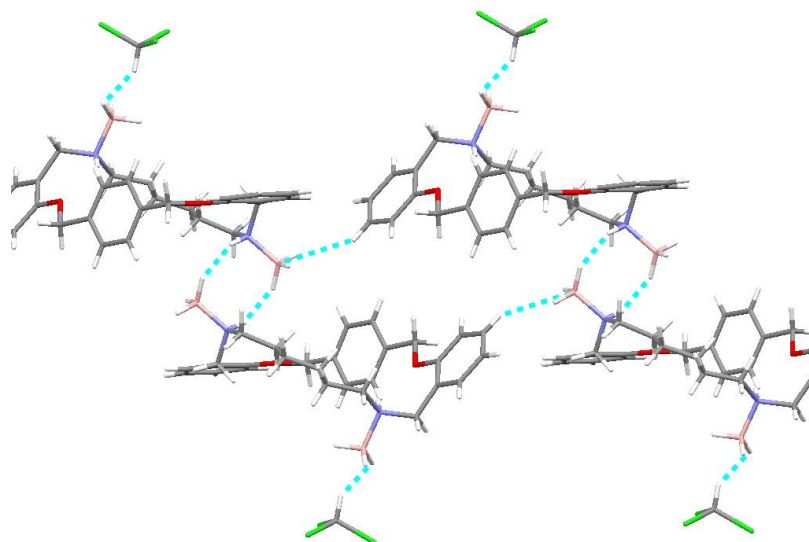**Figure 5.** Intermolecular array in the lattice of **3**.

Figure 6. Chain of dimers linked by C-H···H-B hydrogen bonds.

The stability of compound **3** to hydrolysis is undoubtedly the result of the N-H···H-B and C-H···H-B dihydrogen bonds formation because this array induces an effective spatial isolation of the N-B bond, which is almost covered by a hydrophobic ambient.

Conclusions

The unconventional N-H···H-B and C-H···H-B dihydrogen bonds and the C-H···π interactions play an important role in determining the supramolecular array in the crystal structure of the oaxaazacyclophane-borane adduct and they all influence the stability of this compound to hydrolysis.

Experimental Section

General Procedures. All solvents and reagents were used as received without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded with Varian INOVA 400 and 500 or Bruker AVANCE-400 spectrometers using TMS and BF_3-OEt_2 as standard references. Infrared spectra were obtained in solid KBr using a FT-IR Perkin Elmer Spectrum GX. Cold electrospray mass spectrometric measurements were performed with a JEOL JMS 700 equipment, cooling the supply tube with dry ice.

Elemental analyses were carried out on a Perkin-Elmer series II 2400 instrument. Elemental analysis for carbon was not satisfactory. Elemental analyses of boron derivatives are particularly

complicated because of the production of incombustible residues and are, therefore, not always in the established limits of exactitude, especially with respect to carbon.[11]

X-ray diffraction studies were performed with a BRUKER-AXS APEX diffractometer with a CCD area detector (0.71073 Å, monochromator: graphite). Frames were collected via ω-rotation at 10 s per frame (SMART[12a]). The measured intensities were reduced to $F2$ and corrected for absorption with SADABS (SAINT-NT[12b]). Structure solution, refinement, and data output were achieved with the SHELXTL-NT. Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in geometrically calculated positions using a riding model. The molecular and crystal structures were created by the BRUKER SHELXTL and MERCURY software packages.[12c,13] Details of the crystal structure determination and solution refinement: colorless prism with dimensions $0.525 \times 0.5 \times 0.275$ mm, $M = 345.87$, Triclinic, *P-1*, a=10.3152(10), b=10.9207(11), c=15.6942(16) Å, $\alpha = 110.262(2)$, $\beta = 98.274(2)$, $\gamma = 101.512(2)°$, V = 1580.9(3) Å^3, Z = 2, $T = 293(2)$ K, $\rho_{calc} = 1.213$, $F(000) = 612$, $\mu = 0.318$ mm^{-1}, $\lambda = 0.71073$ Å; 4128 total independent reflections measured, 3046 reflections observed with $I \geq 2\sigma(I)$; number of parameters refined = 367, $R = 0.0893$, goodness of fit = 1.197. Crystallographic data for **3** have been deposited at the Cambridge Crystallographic Data Center as CCDC No 650762. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

2,6-Dioxa-9,16-diaza-1,3(1,2),4(1,4)-tribenzenacycloheptadecaphane-borane (3). 60 mg (0.15 mmol) of Schiff base (**1**) and 6 mg (0.29 mmol) of LiBH$_4$ were dissolved in 10 mL of dry THF and stirred at 60°C during 7.5 h, and then at room temperature overnight. After this time, water was added and gas liberation was observed. Solvents were evaporated using air, and a chloroform-water extraction was performed. A white solid matter was recovered after the organic phase was evaporated. Yield, 44 mg (93%), m.p. 162-164 ºC. ^{1}H NMR (CDCl$_3$) δ (ppm) = 7.53 (m), 7.38 (m), 7.32 (bs), 7.04 (m), 5.15 (m), 3.92 (m), 2.62 (m), 1.70 (s), 1.38 (m), 1.10 (m) NMR ^{13}C δ (ppm) = 156.7 (*Ci*-O), 136.5 (O-CH$_2$-*Ci*), 132.5 (NH-CH$_2$-C*i*-*CH*), 132.4 (NH-CH$_2$-C*i*-*CH*), 130.1 (O-C*i*-CH-*CH*), 128.8 (O-CH$_2$-C*i*-*CH*), 128.4 (O-CH$_2$-C*i*-*CH*), 122.9 (NH-CH$_2$-*Ci*), 122.9 (NH-CH$_2$-*Ci*), 121.6 (NH-CH$_2$-C*i*-CH-*CH*), 111.2 (O-C*i*-*CH*), 70.0 (O-*CH$_2$*-C*i*), 57.6 (NH-*CH$_2$*-C*i*), 57.4 (NH-*CH$_2$*-C*i*), 55.6 (NH-*CH$_2$*-CH$_2$), 54.5 (NH-*CH$_2$*-CH$_2$), 30.9 (NH-CH$_2$-*CH$_2$*), 26.3 (NH-CH$_2$-CH$_2$-*CH$_2$*). IR (KBr): υ (cm^{-1}) = 3282 (w), 3267 (w), 2962 (w), 2921 (s), 2854 (m), 2390(s), 2271(s), 1603 (m), 1589 (m), 1495 (m), 1455 (m), 1422 (m), 1289 (m), 1238 (s), 1198 (m), 1163 (m), 1118 (m), 1017 (s), 813 (m), 758 (s). FAB$^+$: m/z = 458 (M$^+$,5), 445 (M$^+$-BH$_3$, 55). Elem. anal. Calcd for C$_{28}$H$_{40}$B$_2$N$_2$O$_2$ C, 73.39; H, 8.80; N, 6.11, found C, 70.52; H, 9.30; N, 5.76.

Acknowledgements

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