1,6;2,3-Bis-BN-cyclohexane: Synthesis, structure and hydrogen release

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Supporting Information Placeholder

ABSTRACT: BN/CC isosterism has been widely investigated as a strategy to expand carbon-based compounds. The introduction of BN units in organic molecules always results in novel properties. In this work, we reported the first synthesis and characterization of 1,6;2,3-bis-BN cyclohexane, an isostere of cyclohexane with two adjacent BN pairs. Its ring flipping barrier is similar to that of cyclohexane. Protic hydrogens on N in 1,6;2,3-bis-BN cyclohexane show higher reactivity than its isomeric bis-BN cyclohexane. This compound exhibits an appealing hydrogen storage capability of >9.0 wt%, nearly twice as much as the 1,2;4,5-bis-BN cyclohexane.

Due to the neighboring positions in the periodic table, boron−nitrogen (B−N) bond is isoelectronic with carbon−carbon (C−C) bond. Replacing C−C bonds with B−N bonds, forming BN/CC isostere, has been explored to create molecules featuring different chemical and physical properties.[1] Due to different electronegativity, there is appreciable bond polarity in B−N in comparison with C−C, which is the fundamental reason for the distinct properties in the BN-containing compounds than their carbonaceous counterparts.[2-4] For example, hexagonal boron nitride is insulating while graphite is highly conducting.[5, 6] BN-containing chemicals show promising potential in many fields of applications, such as bioactive agents,[7-10] hydrogen storage,[11-18] and functional materials.[19-26] Among these, cyclic BN-containing compounds have received considerate attentions due to their tunable properties. [27-32]

One exemplary case of BN/CC isosterism can be seen from cyclohexane and its BN derivates. In 1,2-BN cyclohexane (Figure 1, **A**) one C−C bond is replaced by B−N.[33] Compared with cyclohexane, 1,2-BN cyclohexane features reduced activation barrier for ring inversion. Dehydrogenation of 1,2-BN cyclohexane under thermal activation leads to trimerization. In another BN isostere of cyclohexane, 1,2;4,5-bis-BN cyclohexane (Figure 1, **B**),[34] two B−N bonds are separated by individual carbon atoms. This compound releases hydrogen at room temperature with a ruthenium complex as the catalyst. **B** can be an ef-

fective precursor to form a graphene-like boron-carbon-nitrogen monolayer with homogeneous stoichiometry, which can be a useful material for electronic applications.[35] Despite their significance in fundamental chemistry and materials science, the reported BN/CC isosteres are still limited, which is likely due to the difficulties in synthesis.[36, 37] The co-existence of hydridic and protic hydrogens make cyclic BN compounds highly reactive, so their purification and isolation can be challenging.
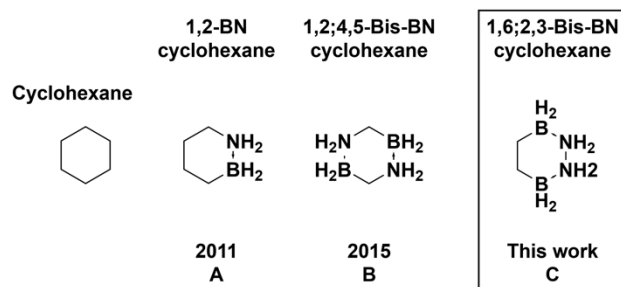

Figure 1. Cyclohexane and its BN isosteres.

There exist many combinations in numbers and positions of B−N bonds relative to C−C or B−N in the substituted carbonaceous compounds. For example, in BN isosteres of cyclohexane with two BN units, there can be different arrangements of B−N bonds such as B−N−N−B, N−B−B−N, B−N−B−N, B-N-C-N-B and B−N−C−B−N. Inspired by the high hydrogen capacity and the curiosity into potential exotic properties, we decided to synthesize BN isosteres of cyclohexane with B−N−N−B (1,6;2,3-bis-BN cyclohexane, **C**). Heteroatomic connectivity will affect the stability and reactivity of BN-containing compounds. According to our computational results, the free energy of **C** is much higher than that of bis-BN cyclohexane, with a difference of ~43.0 kcal/mol at G3B3 (Table S1). This high free energy indicates potential high reactivity of **C**, which makes synthesis challenging. Meanwhile, we expect **C** to release hydrogen under milder conditions, in comparison to **B**, which releases hydrogen merely above 200 ℃ in the absence of catalysts.[34] In this

work, we report the first synthesis of 1,6;2,3-bis-BN cyclohexane (Figure 1, **C**), the first BN/CC isostere of cyclohexane with two adjacent BN fragments. **C** thermally releases hydrogen starting from ~100 °C, or catalytically in acetonitrile at room temperature.

Scheme 1. Synthesis of 1,6;2,3-bis-BN cyclohexane

1,6;2,3-bis-BN cyclohexane
42% over two steps
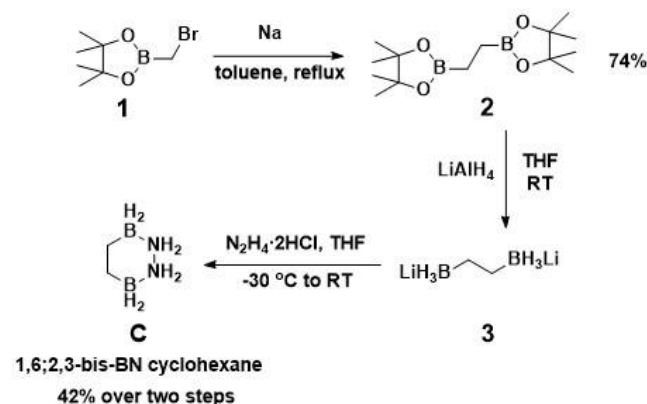
As illustrated in Scheme 1, starting from compound **1**, 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **C** was synthesized in three steps. Following the method reported by Srebnik and co-workers,[38] **1** was first converted to **2** with a yield of 74%. A reduction reaction then led to the formation of **3**, which subsequently reacted with hydrazine dihydrochloride to give the desired product. **C** was isolated *via* chromatography and crystallization with an overall yield of 42%. The structure of **C** was confirmed by nuclear magnetic resonance (NMR) spectroscopy (Figure S1-S4), elemental analysis and single-crystal X-ray diffraction analysis (Table S2-S7). To the best of our knowledge, **C** is the first BN isostere of cyclohexane with two adjacent BN units, whose structure is shown in Figure 2.
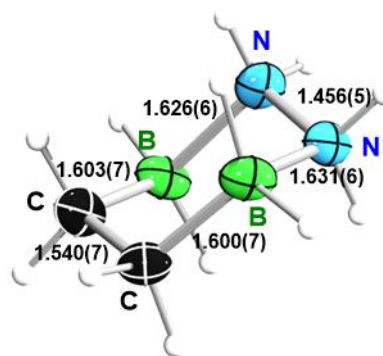

Figure 2. Crystal structure of 1,6;2,3-bis-BN cyclohexane. Thermal ellipsoids are drawn at the 50% probability level.

C adopts a chair conformation in the solid state similar to cyclohexane, **A**,[33] and **B**.[34] All hydrogen atoms can be found on the residue density map. The B–C, C–C, B–N, N–N bond lengths all lie in the expected ranges for the corresponding single bonds. The B–N bonds of **C** (av. 1.63 Å) are slightly longer than those of **A** (1.6140(12) Å) and **B** (1.5959(11) Å). The C–B bonds of **C** (av. 1.60 Å) are consistent with that of **A** (1.6088(12) Å) and **B** (av. 1.61 Å). The N–N bond of 1.456(5) Å in **C** is slightly shorter than that of the acyclic hydrazine-borane adduct $H_3BNH_2NH_2BH_3$ (1.470 Å)[39]. (See Table S8 for comparison).

We studied if the B–N–N–B linkage in **C** affects the conformational dynamics in comparison with other isosteres. Variable temperature NMR experiments were therefore conducted (Figure 3). At 273 K, ^{1}H NMR spectrum showed a sharp signal at 6.87 ppm for the NH_2 unit. The rate of ring flip slowed down as the temperature was lowered. At 213 K, the diastereotopic NH protons become non-exchangeable on the NMR time scale, thus leading to two distinguishable ^{1}H signals. The coalescence happened at ~230 K. The free energy for activation ($\Delta G_{(C)}^\ddagger$) of **C** from chair to twisted boat interconversion is estimated[40] to be 10.1 kcal/mol (Table S9), which is comparable to that of cyclohexane (10.5 kcal/mol), but higher than that of 1,2-BN cyclohexane (8.8 kcal/mol).[33] The difference in the ring flipping energy barrier is likely related to the bond lengths of the ring skeleton.[33, 41, 42] For instance, longer B–N bond of 1,2-BN cyclohexane (1.6140(12) Å) than C–C bonds in cyclohexane (1.51 to 1.53 Å) (Table S8) should reduce the ring strain and steric hindrance, resulting in a lower flipping energy barrier.[33, 41, 42] In our case, **C** possesses two longer (B–N 1.626(6) Å and 1.631(6) Å) but one shorter (N–N bond 1.456(5) Å) bonds with respect to the cyclohexane skeleton, which combined leads to a flipping energy barrier comparable to that of cyclohexane.
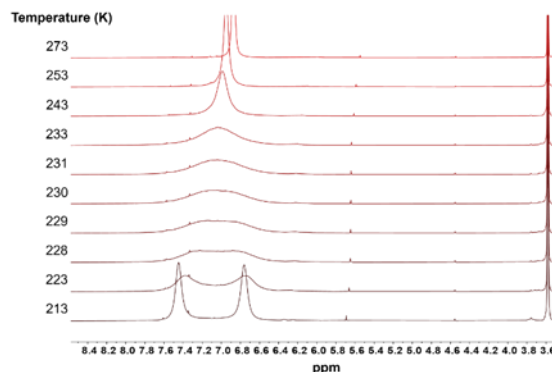

Figure 3. 400 MHz ^{1}H NMR signal of the NH_2 group of **C** in THF-d8 at different temperatures.

The physical and chemical properties of **C** are quite different from its isosteres, including cyclohexane, **A**, and **B**. For instance, **C** is a white solid at room temperature, whose rapid decomposition with heating stopped us from getting its melting point. **C** slowly reacts with moisture in air with >95 % conversion within 43 h (Figure S5–S7). In stark contrast, cyclohexane and 1,2-BN cyclohexane are inert to moisture, and their melting points are 6.47 °C and 62–63 °C, respectively.[33] Meanwhile, **B** sublimes at temperatures between 150 °C and 200 °C, and has good stability to moisture.[34] In addition, **C** decomposes slowly in the anhydrous aprotic solvent at room temperature, with a complete decomposition taking around 22 days in THF and 29 days in acetonitrile, respectively (Figure S8–S13). In contrast, **A** and **B** are stable in aprotic solvents and inert to water.

The co-existence of hydridic H(–B) and protic H(–N) typically enables facile hydrogen formation under mild conditions.[33, 34, 43-46] As an organic derivative of ammonia borane, compound **C** catches our attention due to its high hydrogen capacity. If all the eight nitrogen- and boron-bound hydrogens of **C** are available for H_2 release, 1 eq. compound **C** can release 4 eq. H_2, meaning a hydrogen storage capability of 9.4 wt%. We investigated its hydrogen release under two different conditions. First, we studied its catalytic dehydrogenation in solvents at room temperature. After numerous attempts, the hydrogen release was only around 1.47 eq. from 1 eq. compound

C when Pt/C was used (Table S10 and Figure S14), far less than 4 eq. Then we resorted to thermal dehydrogenation.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to investigate the dehydrogenation progress by heating to 600 °C. As shown in Figure 4**a**, the first weight loss was exothermic which started at about 100 °C and ended at about 180 °C. When dwelled at 180 °C, ~9.55 wt% weight loss was observed (Figure 4**b**). Temperature programmed desorption-mass spectra (TPD-MS) results (Figure S15 and S16) indicated that gases released before 180 °C were predominantly H_2 with trace amounts of diethyl ether and pentane (residual from the preparation), nitrogen and ammonia. This is why the actual weight loss was higher than the theoretical hydrogen capacity of 9.4 wt%. For temperatures higher than 180 °C, traces amount of diborane, methane, ethane and nitrogen were observed, indicating the slight decomposition of the six-membered rings.
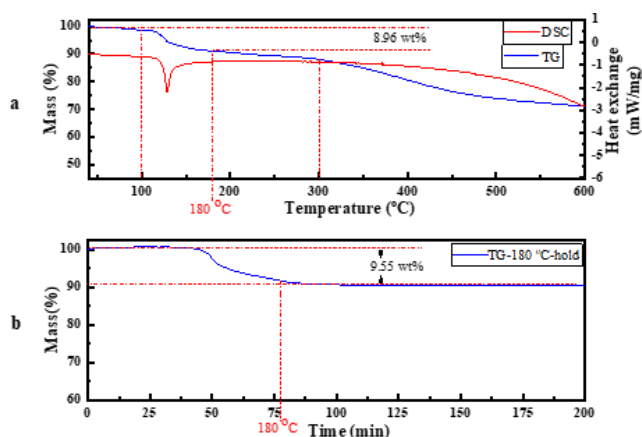

Figure 4. TGA/DSC results with (a) heating to 600 °C and (b) heating to 180 °C with a 2 h dwell.

We also investigated the dehydrogenation products obtained after heating at 140 °C and 180 °C for 2 hours *via* FTIR. There are typical NH stretching (3245 - 3113 cm^{-1}), NH bending (1582 cm^{-1}), BH stretching (2326 to 2219cm^{-1}), BH torsion (1166 and 1126 cm^{-1}), CH stretching (2909 - 2791 cm^{-1}), and BN stretching (1368, 764 and 700 cm^{-1}) in the IR spectra (Figure S17) of **C**.[47] Intensities of N–H and B–H bands decreased with heating while B–N band became stronger. Based upon solid state ^{11}B NMR spectra (Figure S18), **C** first transformed into intermediates consisting of both sp^2 and sp^3 B, and finally mainly sp^2 B with a broad signal typically observed for hydrogen-free BN units.[18] Solid state ^{1}H NMR (Figure S19) and ^{13}C NMR spectrum (Figure S20) of final dehydrogenated products show signals related to CH_2 which is consistent with FTIR results. This phenomenon indicates that H_2 formation is likely driven by (N–)H···H(–B) dihydrogen bond interactions with the subsequent formation of B–N bond, which is consistent with previous studies.[16] We were unable to isolate crystals of intermediates from the dehydrogenation mixture.
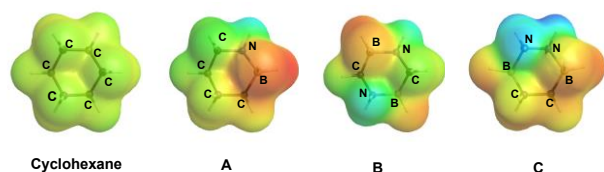

Figure 5. Electrostatic potential calculated at M062X/6-31+G(d) mapped on the electron density isosurface [-0.08

0.15]: Blue refers to the positive regions; red refers to the negative regions. The unit for electrostatic potential is a.u.

B only releases a limited amount of hydrogen *via* thermal activation, and the hydrogen capacity of **C** is nearly double of **B**, which releases 4.7 wt% H *via* catalysis in solvent (Table S11). To understand the underlying reason for the difference, we conducted computational studies on these cyclohexane-like structures. The electrostatic potential calculated at M062X/6-31+G(d) (Figure 5) shows that the regions around NH fragments in **C** bear more positive electrostatic potential, while the negative potential regions of BH fragments are similar among these BN cyclohexane isomers. Hs on N in **C** are more positively charged compared those in **B**, as indicated by the Merz-Singh-Kollman charge analysis (Figure S21). As a result, stronger dihydrogen bond interactions are expected in **C** which leads to dehydrogenation at lower temperatures for **C** in comparison with **B**. This is also consistent with the calculated proton affinities and hydride affinities (Table S12).

The final dehydrogenation product is polymeric and has poor solubility in solvents, and therefore we have not been able to decipher its exact structure (Figure S22-24). Based on FTIR, NMR and TGA results, we believe the dehydrogenation product is a polymeric product with an empirical formula of $C_2N_2B_2$ H_n(n < 4.3). In the compound, nearly all the hydrogens are linked to carbon atoms. Currently, the most widely applied regeneration from BN based polymeric product involves a digestion reaction to form -NH$_x$ followed by a reduction reaction to form -BH$_x$. The current regeneration involves three steps, including alcoholysis, reduction using LiAlH$_4$ and cyclization using hydrazine salt (Figure S25 and S26). The overall yield is about 52%. However, this method is expensive and not practical for large scale applications. Inspired by other work related to regeneration,[48, 49] more research is needed to develop a cost-effective and sustainable regeneration method. Compared with ammonia borane, **C** releases considerable amount of H_2 without induction and does not foam during thermal decomposition. **C** can be regenerated under relative mild conditions with good efficiency.

In summary, we prepared a novel BN isoelectronic isomer of cyclohexane, namely 1,6;2,3-bis-BN cyclohexane, and investigated its properties. It adopts the same chair conformation in the solid state as cyclohexane. Replacing four CH_2 fragments with $-BH_2-NH_2-NH_2-BH_2-$ does not obviously affect the energy barrier for the ring flip of this six-member ring structure. **C** shows excellent capability for hydrogen release. Under thermal activation, it released > 9.0 wt% H, which is about twice of other isoelectronic BN cyclohexane. This work demonstrates the potential of BN/CC isosterism in creating novel molecules with unique properties.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectroscopic data, additional computational details and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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LiH$_3$B—⟍—BH$_3$Li

+

N$_2$H$_4$·2HCl

−LiCl; −H$_2$ →

H$_2$B—NH$_2$—NH$_2$—B—H$_2$

1,6;2,3-bis-BN cyclohexane

> 9.0 wt% hydrogen release capability