**Utilising the combined power of theory and experiment to understand molecular structure – Solid-state and gas-phase investigation of morpholine borane**

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**Abstract**

The molecular structure of morpholine borane complex has been studied in the solid-state and gas-phase using single-crystal X-ray diffraction, gas electron diffraction and computational methods. Despite both the solid-state and gas-phase structures adopting the same conformation, a definite decrease in the B–N bond length of the solid-state structure was observed. Other structural variations in the different phases are presented and discussed. To explore the hydrogen storage potential of morpholine borane, the potential energy surface for the uncatalysed and BH3-catalysed pathways, as well as the thermochemistry for the hydrogen release reaction, were investigated using accurate quantum chemical methods. It was observed that both the catalysed and uncatalysed dehydrogenation pathways are favourable with a barrier lower than the B–N bond dissociation energy thus indicating a strong propensity for the complex to release a hydrogen molecule rather than dissociate along the B–N bond axis. A minimal energy requirement for the dehydrogenation reaction has been shown. The reaction is close to thermoneutral as demonstrated by the calculated dehydrogenation reaction energies thus implying that this complex could demonstrate potential for future on-board hydrogen generation.

**Introduction**

The morpholine borane complex (**MBC**, Figure 1) has been known for several decades,[1] is commercially available, and has many applications in synthetic chemistry[2-6] as a reducing agent for advanced materials coating[7-9] as well as its potential hydrogen storage capability.[10] However, its crystal structure has not been reported or deposited in the Cambridge Structural Database (CSD)[11] and its gas-phase molecular structure is also not known. The latter is perhaps not surprising; amine-boranes generally have very low vapour pressures,[12] making them difficult to study using gas electron diffraction (GED) or microwave spectroscopy (MWS). By using nuclear magnetic resonance (NMR) spectroscopy to study the effect of nitrogen-borane coordination on the ring conformational equilibrium of **MBC**, a preferred equatorial conformation of **MBC** was identified.[13] The structure of the precursor, morpholine, has been reported both in the solid state[14] and gas phase.[15-16] Structurally-related compounds such as borane complexes of morpholine-4-carboxy,[17] (*R*)-3-morpholino-1-phenyl-1-propanol,[18] *N*-(trimethylsilyl)morpholine[19] as well as valenceisoelectronically similar thiomorpholine borane[20] have all been characterised by single-crystal X-ray diffraction (XRD).

Amine borane complexes including **MBC** are projected as potential candidates for on-board chemical hydrogen storage applications due to the presence of protic N–H and hydridic B–H bonds which may lead to the formation of dihydrogen bonds.[21-25] Recently,[10] the hydrogen storage capability of **MBC** has been demonstrated *via* hydrolysis using *in-situ*-generated silver and palladium nanoparticles as catalysts. While success had been recorded in identifying amine borane complexes that can release molecular hydrogen under mild conditions,[26-28] regenerating the complexes from the spent fuel remains a major challenge to researchers due to the unfavourable regeneration pathways.[21] There has also been disagreement with regards to the mechanism of thermal dehydrogenation of these systems. By using coupled cluster CCSD(T) calculations, Nguyen *et al.[29]* concluded that a number of transition states are involved in the thermal dehydrogenation of ammonia borane, highlighting the role of BH3 as a bifunctional catalyst in a favourable dehydrogenation pathway.

Correlating thermochemical properties with the structural parameters of **MBC** such as the length of the essential B–N bond will enable the design of new materials with promising attributes. Given the potential for hydrogen storage that **MBC** presents, and considering the lack of structural information available in the literature, we report herein the molecular structures of **MBC** in both the solid-state and gas-phase. We also investigate the thermochemistry and reaction energy pathways related to the hydrogen release reactions. Thus we are able to explore the energy requirements for future on-board hydrogen generation using this complex. Complete structural solutions in the solid state (*via* XRD) and gas phase (*via* GED) are presented and discussed along with the dehydrogenation reaction pathways and thermochemistry of the dehydrogenation process.

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Figure 1: The lowest-energy ground-state molecular structure of **MBC** in the gas-phase showing atom numbering.

**Experimental and Theoretical Methods**

**Gas Electron Diffraction**

GED data were acquired using the University of York gas electron diffractometer.[30] An accelerating voltage of around 42.2 keV was used, giving an electron wavelength of approximately 6.0 pm. Electron-sensitive image plates (Fuji BAS-IP MS 2025) were used to record the scattering intensities. Sample/nozzle temperatures and nozzle-to-image-plate distances are given in the Supporting Information (Table S1). A flatbed image-plate scanner (Fuji BAS-1800II) was used to digitise the scattering intensities. The digitised scattering intensities were reduced to molecular intensity curves (MICs) using an azimuthal averaging routine implemented in the University of York data extraction package *xtract*.[31] The least-squares refinement process was carried out using the ed@ed program (version 2.3)[32] employing the scattering factors of Ross *et al*.[33] Weighting points for the off-diagonal weight matrices, correlation parameters and scale factors are also given in Table S1 while the least-squares correlation matrix for the refinement is provided in Table S2. Further details about the vaporisation are given in the supplementary information.

**Single Crystal X-ray Diffraction**

Single crystals of **MBC** (C4H12BNO, 95%)were used as purchased from Sigma Aldrich. A suitable crystal was selected, coated in perfluoronated PEG and mounted on a nylon loop on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at either 120.0(1) K or 297.9(2) K during data collection. Using Olex2,[34] the structure was solved with the ShelXT[35] structure solution program using Intrinsic Phasing and refined with the ShelXL[36] refinement package using least-squares minimisation. Crystallographic information related to the solution and refinement is given in Table S3. Both data sets can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif. CCDC: 1955455 [120.0(1) K] and 1961181 [297.9(2) K].

Crystal Data at 120.0(1) K: for C4H12BNO (*M* = 100.96 g/mol): monoclinic, space group *P*21/*n* (no. 14), *a* = 6.8632(2) Å, *b* = 11.5032(3) Å, *c* = 8.1150(3) Å, *β* = 105.219(3)°, *V* = 618.20(3) Å3, *Z* = 4, *T* = 120.0(1) K, *μ*(MoKα) = 0.073 mm-1, *Dcalc* = 1.085 g/cm3, 34462 reflections measured (6.938° ≤ 2*Θ* ≤ 83.236°), 4226 unique (*R*int = 0.0519, *R*sigma = 0.0335) which were used in all calculations. The final *R*1 was 0.0481 (I > 2*σ*(I)) and w*R*2 was 0.1510 (all data).

Crystal Data at 297.9(2) K: for C4H12BNO (*M* = 100.96 g/mol): monoclinic, space group *P*21/*n* (no. 14), *a* = 6.9662(5) Å, *b* = 11.5199(8) Å, *c* = 8.2344(6) Å, *β* = 105.678(8)°, *V*= 636.22(8) Å3, *Z* = 4, *T* = 297.9(2) K, *μ*(MoKα) = 0.071 mm-1, *Dcalc* = 1.054 g/cm3, 13775 reflections measured (7.03° ≤ 2*Θ* ≤ 57.972°), 1693 unique (*R*int = 0.1578, *R*sigma = 0.0666) which were used in all calculations. The final *R*1 was 0.0758 (I > 2*σ*(I)) and *wR*2 was 0.2292 (all data).

**Computational Methods**

All electronic structure calculations were carried out using the GAUSSIAN 09[37] and NWChem[38] software suites. NWChem calculations were carried out using the supercomputing resources of the New Zealand eScience Infrastructure (NeSI). To incorporate the effects of electron correlation on the geometrical parameters, a series of calculations involving all the core and valence electrons using second-order Møller-Plesset perturbation theory [MP2(full)][39] were carried out with the 6-31G\*, 6-311G\*, and 6-311+G\*[40-43] basis sets. The convergence of all calculations to minima on the ground-state potential energy surface was verified *via* vibrational frequency analysis.

Analytic second derivatives of the energy with respect to nuclear coordinates were calculated at the MP2(full)/6-311+G\* level to give the Cartesian force fields which were then used with the SHRINK[44-46] program to provide estimates of the amplitudes of vibration (*u*) and perpendicular distance corrections (*k*) for use in the GED refinement.

Transition state structures for the compounds along the dehydrogenation reaction pathways were obtained using the synchronous transit-guided quasi-Newton (STQN) method.[47] For the BH3-catalysed reaction pathway, STQN was not used to predict the transition structure because of the numerous molecules on the pathway. The transition state structure was obtained by normal eigenvalue-following which follows the reaction path from the equilibrium geometry to the transition state structure by specifying which vibrational mode should lead to a reaction given sufficient kinetic energy. To ascertain the identity of the relevant transition state structures, intrinsic reaction coordinate (IRC) calculations[48] were also undertaken at the B3LYP/6-31G\* level. The calculated Cartesian coordinates for all the molecules are provided in Tables S4–S11.

The B–N bond dissociation energy (B–NBDE) and the thermochemical parameters at 298.15 K were calculated using single-point energies obtained at CCSD(T)/CBS level and with the composite CBS-QB3 method,[49] employing total atomisation energies and heats of formation as described by Curtiss *et al*.[50] This method predicts thermochemical properties with chemical accuracy;[51] previous tests reported the mean absolute deviation of less than 5.27 kJ/mol.[52] For the CCSD(T)/CBS method the correlation-consistent aug-cc-pV*n*Z basis sets of Dunning,[53] with *n* = D, T, and Q have been used to extrapolate the CCSD(T) energies to the complete basis set (CBS) limit by use of the mixed Gaussian/exponential expression suggested by Peterson *et al[54]* where *n* = 2 (cc-pVDZ), 3 (cc-pVTZ) and 4 (cc-pVQZ).

This extrapolation method has been shown to yield atomization energies in close agreement with experiment as compared to other extrapolation approaches up through *n* = 4. The calculated energies and corrections for enthalpy (H), Gibbs Free Energy (G) and Zero Point energies used in the calculation of the thermochemical properties are provided in Tables S12 and S13.

**Results and Discussion**

***Ab initio* molecular structure**

The lowest-energy ground-state structure of **MBC** on the potential energy surfaces featured an equatorial chair-like conformation with *C*s symmetry. The geometric parameters obtained at the MP2(full) level, employing different basis sets with additional diffuse and polarization functions, are tabulated in Table 1. These parameters are in good agreement with those obtained for other cyclic amine borane systems in the literature.[55-57] The parameters varied only slightly as the basis set was extended. The bond lengths and angles were found to differ by no more than 1 pm and 1°, respectively. The slight variation in the parameters at different levels of theory was used to estimate the flexible restraints[58-60] which were employed in the least-squares refinement of the GED data.

Table 1: Selected optimised structural parameters for **MBC** calculated at the MP2(full) level of theory with different basis sets.

|  |  |  |  |
| --- | --- | --- | --- |
| **Parameter**A | **MP2(full)/6-31G\*** | **MP2(full)/6-311G\*** | **MP2(full)/6-311+G\*** |
| *r*B–N | 163.9 | 163.1 | 163.2 |
| *r*N–C | 148.4 | 148.3 | 148.3 |
| *r*C–C | 151.7 | 151.8 | 151.8 |
| *r*N–H | 102.6 | 102.0 | 102.2 |
| *r*B–H av | 121.2 | 121.4 | 121.5 |
| *r*C–H av | 109.5 | 109.4 | 109.5 |
| *r*C–O | 142.3 | 141.6 | 141.8 |
| *r*O…N | 286.9 | 287.7 | 287.9 |
| ∠N–B–H av | 104.9 | 105.4 | 105.4 |
| ∠C–N–B | 112.4 | 112.5 | 112.6 |
| ∠C–C–N | 111.0 | 111.1 | 111.2 |
| ∠O…N–B | 152.8 | 152.5 | 153.0 |
| φC–C–N–B | –178.8 | –178.2 | –178.8 |

A Bond lengths in pm; bond angles and torsion angles in °.

**GED structure refinement**

A structural model based on the MP2(full)/6-311+G\* calculations, possessing 18 independently-refinable parameters and 1 dependent parameter, was used in a SARACEN *r*h1-type refinement.[58-60] All the parameters were refined with flexible restraints being applied to 16 of the 18 independently-refinable parameters that could not be refined freely. Amplitudes of vibration (*u*h1) and curvilinear corrections (*k*h1) for each atomic pair generated from the theoretical Cartesian force fields by use of the SHRINK program were incorporated into the refinement in order to account for the structural shrinkage usually observed in a GED analysis.[44-46] All relevant vibrational amplitudes were refined and are reported in Table S14. The level of agreement between the theoretical model and the experimental GED data can be assessed qualitatively by inspection of the radial distribution curve shown in Figure 2. The molecular intensity curve (MIC) is provided in Figure S1. The refinement resulted in a goodness-of-fit factor (*R*G) of 4.92% indicating an excellent fit of the theoretical model to the experimental data thereby giving confidence as to the accuracy of both the experimental and theoretical methods used in this refinement.

Selected refined (*r*h1) and calculated (*r*e) geometric parameters, as well as the applied flexible restraints, are shown in Table 2 with the full list of refined structural parameters provided in Table S15. In general, the experimental and theoretical parameters agree with each other within reason except for *r*O…N. In particular, the dative B–N distance [GED 164.4(6) pm; MP2(full)/6-311G\* 163.2 pm] differed by only 1.2 pm and is very similar to those distances reported for other amine-borane complexes. For instance, the B–N distance for methylamine borane [MeH2N–BH3, *r*h1B–N = 163.3(7) pm] and dimethylamine borane [Me2HN–BH3, *r*h1B–N = 164.2(4) pm][61] as well as the theoretical B–N value for piperidine borane also with a six-membered ring [C5H11N–BH3, *r*eB–N = 162.9 pm][56] obtained at M06-2X/aug-cc-pVTZ level of theory also fall within a similar range. The reported B–N distance for the single-crystal X-ray diffraction analysis of *N*-borane-*N*-(trimethylsilyl)morpholine [C4H8ON(SiMe3)–BH3] is 163.9(2) pm[19] which is identical to our recently determined GED B–N value for piperidine borane [C5H11N–BH3, *r*h1B–N = 163.9(5) pm].[62] We have also reproduced this experimental B–N distance exactly at the CBS–QB3 level of theory.



Figure 2: Experimental radial distribution and difference (experimental minus theoretical) curves for the GED refinement of **MBC**. Before Fourier inversion, the data were multiplied by *s***·**exp(–0.00002*s*2)/(*Z*C – *f*C)(*Z*O – *f*O).

Finding an accurate B–N distance is important because it has been demonstrated that dehydrogenation of these systems occurs across the B–N bond in a favourable reaction pathway.[63] It is not surprising that *r*O…N differs by 3.3 pm from the theoretical value since it is a non–bonded distance which lies on the symmetry axis and therefore is open to variation due to cumulative subtle differences in bond lengths, bond angles and torsions across the morpholine ring. It is also important to note that *r*C–O was defined in the refinement as a dependent parameter as it was not used in the construction of the molecular model prior to the refinement due to the overall *C*s symmetry of the complex.

Table 2: Selection of refined (*r*h1) and calculated (*r*e) geometric parameters for **MBC**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Parameter**A | **MP2/6–311+G\***  **(*r*e)** | **GED**  **(*r*h1)** | **Restraint** |
| *r*B–N | 163.2 | 164.4(6) | 163.2(9) |
| *r*N–C | 148.3 | 148.2(2) | 148.3(2) |
| *r*C–C | 151.8 | 152.0(6) | – |
| *r*O…N | 287.9 | 291.2(4) | 287.9(5) |
| *r*C–OB | 141.8 | 142.8(5) | – |
| ∠C–N–B | 112.6 | 113.6(3) | – |
| ∠C–C–N | 111.2 | 111.2(2) | 111.2(2) |
| ∠O…N–B | 153.0 | 153.6(5) | 153.0(5) |
| *φ*C–C–N–B | –178.8 | –180.3(5) | –178.8(6) |

A Bond lengths in pm, bond angles and torsion angles in °; figures in parentheses are the estimated standard deviation of the last digits expressed as 2*σ*.

B *r*C–O is a dependent parameter.

Analysis of the solid-state and gas-phase structures of free morpholine (**MP**) determined by single-crystal X-ray diffraction analysis[14] and microwave spectroscopy[16] (MWS) enabled comparison of the structural differences arising from the complexation. These structural changes are shown in Table 3. Bond shrinkage in solids such as the single crystal XRD bond lengths of **MP** are usually observed when comparing to gas-phase structures (as in the MWS values of **MP**) because XRD determines distances between the centres of electron density distribution while MWS and GED determine internuclear distances.[64] With the exception of the non-bonding *r*O…N, the internuclear distances in the MWS results for **MP** are comparable to the values reported here for **MBC** though with a slight change in the geometry upon the formation of the adduct. This is important, keeping in mind that both the MWS and GED take place in the gas phase. The elongation of *r*O…N distance (by 6.9 pm and 3.4 pm for the GED and XRD values respectively) and the widening of ∠C–C–N angle (by 4.4°) upon complexation can be rationalized by the steric effects resulting from the addition of BH3 on the ring, in accordance with the valence shell electron pair repulsion (VSEPR) model.[65-67] Conversely, the structure of the BH3 moiety is seen to change significantly upon complexation with morpholine. The theoretical structure of BH3 would have a trigonal planar configuration (*D*3h). Upon the formation of the complex, pyramidalization of the borane unit occurs, giving an approximately tetrahedral configuration with the hybridization at the boron atom changing from sp2 to sp3.[68] This is consistent with the changes observed in the trimethylamine adducts of borontrifluoride (Me3N–BF3) and borontrichloride (Me3N–BCl3)[69] as well as in trimethylmethylphosphine–borane (MeH2P–BH3).[70]

Table 3: Comparison of main structural parameters for **MP** and **MBC**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Parameters**A,B | **MP** | | **MBC** | |
| **MWS[16]** | **XRD[14]** | **GED** | **XRD** |
| *r*N–C | 147.0 | 146.8(2) | 148.2(2) | 148.6(8) |
| *r*C–C | 152.4(5) | 151.6(3) | 152.0(6) | 150.9(9) |
| *r*C–O | 144.2(7) | 143.2(2) | 142.8(5) | 142.4(8) |
| *r*O…N | 284.3(6) | – | 291.2(4) | 287.7(7) |
| ∠C–C–N | 107.8 | 108.4(18) | 111.2(2) | 111.2(5) |

A Bond lengths in pm, bond angles in °; figures in parentheses are the estimated standard deviation (ESD) of the last digits.

B Bond lengths and angles without ESDs were fixed at their standard values.

**Single crystal structure**

The single-crystal structure of **MBC** collected at 120.0(1) K is shown in Figure 3 while salient geometrical parameters obtained from the crystal structure are tabulated in Table 4 and full parameters are provided in Tables S4 and S5. Due to the high resolution of the data, the absence of any heavy elements and the resulting high data/parameter ratio, all atoms in the structure were refined positionally, without restraints. The thermal parameters of the non-hydrogen atoms were refined anisotropically, but the thermal parameters of the hydrogen atoms were modelled as 1.5x those of the riding atom. **MBC** crystallised in a monoclinic *P*21/*n* unit cell similar to thiomorpholine–borane[20] while *N*-borane-*N*-(trimethylsilyl)morpholine[19] also crystallises in the same space group (*P*21/*c*). However, **MBC**’s precursor (**MP)**[14] crystallised in orthorhombic *P*212121 space group despite sharing the same ring. Unlike the gaseous structure, the crystallographic symmetry elements do not describe intramolecular symmetry. However, the crystal structure does not deviate greatly from the structure it assumes in the gas-phase and the BH3 group is also situated equatorially relative to the ring. Compared with the structure of the free molecule in the gas, shortening of the bond lengths is observed especially the dative B–N distance (by 3.9 pm) and the non-bonding *r*O…N distance (by 3.5 pm) while *r*N–C and *r*O–C bond lengths in both solid state and gas-phase are similar within experimental uncertainties. Data were also collected at 297.9(2) K to evaluate the effect of increase in temperature on the bond lengths. The B–N bond was not found to deviate between temperatures. The shortening can also be attributed to the effects of packing and dipole moments in solids. For angles, the notable difference is the narrowing of the angles O(11)…N(1)–B(4) and C()–N–B(4), both by 1.7°. These structural differences have also been observed in the single crystal structures of linear amine boranes[61] when compared to their gas-phase structures.



Figure 3: 50% probability thermal ellipsoid plot of the extended coordination sphere of **MBC**. Hydrogen atoms are shown as spheres of arbitrary size.

Table 4: Refined geometric parameters for the single crystal structure of **MBC**.

|  |  |
| --- | --- |
| **Parameter**A | **XRD** |
| *r*B(4)–N(1) | 160.5(9) |
| *r*N(1)–C(2) | 148.6(8) |
| *r*N(1)–C(3) | 148.5(8) |
| *r*C(2)–C(8) | 150.9(9) |
| *r*C(3)–C(5) | 151.3(10) |
| *r*C(8)–O(11) | 142.4(8) |
| *r*C(5)–O(11) | 142.6(9) |
| *r*O(11)…N(1) | 287.7(7) |
| ∠C(2)–N(1)–B(4) | 111.9(5) |
| ∠C(3)–N(1)–B(4) | 112.7(5) |
| ∠C(8)–C(2)–N(1) | 111.2(5) |
| ∠C(5)–C(3)–N(1) | 111.5(5) |
| ∠O(11)…N(1)–B(4) | 151.9(3) |

A Bond lengths in pm, bond angles in °; figures in parentheses are the estimated standard deviation (ESD) of the last digits expressed as 2*σ*.

Both sets of data were analysed to evaluate the short H…H contacts. In the structure collected at 120.0(1) K the H…H contacts between the protic H (attached to N of one **MBC**) and hydridic H (attached to B of another **MBC**) are slightly shorter than the H…H contact along the B–N bond axis. In the 297.9(2) K structure, the H…H interaction along the axis of the B–N bond is slightly shorter than the interaction between the protic H (attached to N of one **MBC**) and hydridic H (attached to B of another **MBC**). This demonstrates a trend of **MBC** molecules moving further apart as the temperature increases, and therefore the dehydrogenation is more likely to occur along the axis of the B–N bond than between molecules, as the intramolecular interaction remains the same as the temperature increases but the intermolecular interaction becomes less favourable.

**Reaction energy pathway and thermochemical properties**

To understand the mechanism of the hydrogen release reactions for this system, which is hypothesized as a potential candidate for chemical hydrogen storage, we explored two reaction channels (displayed in Figure 4) towards the unimolecular dehydrogenation using the accurate CBS-QB3 method.[49] Bond lengths in the molecules and transition structures that are essential to the hydrogen release reactions are presented in Table 5. The first channel is the dehydrogenation of **MBC** to give the dehydrocoupled product **MBC–P** (Figure 5). A transition structure (**MBCTS1**, Figure 6) was located at the saddle point connecting **MBC** and **MBC–P** using the STQN approach.[47] This pathway has an activation barrier of 166 kJ/mol to produce a low-lying and more stable **MBC–P** with a lower energy of –19 kJ/mol relative to the reactant **MBC**. In the **MBCTS1** structure, N–H and B–H bonds are elongated by 39.4 pm and 17.7 pm relative to **MBC**. This results in the formation of a H…H dihydrogen bond[71] having a theoretical distance of 97.3 pm. Formation of dihydrogen bonds has previously been considered to occur prior to the release of a hydrogen molecule.[12, 24, 72-73] This mechanism is favourable considering the fact that the barrier is lower than the B–N bond dissociation energy (B–NBDE) predicted at CBS–QB3 (Table 6) for this system. However, for all the other cyclic amine boranes and ammonia borane that have been studied so far[29, 56, 74] including our recent work on azetidine-borane,[57] the barrier was higher than the B–NBDE. This situation favours dative bond dissociation over the dehydrogenation, hence employment of a Lewis acid BH3 as a bifunctional catalyst in a favourable mechanism is required.[75] The second channel we investigated involves the use of a Lewis acid BH3 in the dehydrogenation process. Here, we located a lowest-lying condensed structure (**MBC**---**BH3**, Figure 7) on the potential energy surface formed by the interaction between the partial lone pair on the nitrogen atom in **MBC** and an incoming BH3 in a barrier-less fashion at –73 kJ/mol relative to the separated reactants. This intermediate then proceeds to form the transition structure (**MBCTS2**, Figure 8) by reducing the barrier from 166 kJ/mol to 37 kJ/mol. **MBCTS2** features a structure with a theoretical H…H contact of 90.8 pm and N–H and B–H distances elongated by 50.0 pm and 12.7 pm relative to **MBC**. The dihydrogen contact here is more enhanced than in **MBCTS1**. This pathway is the most favourable and further indicates the vital role of BH3 participation as an effective catalyst in the dehydrogenation process as evidenced in other amine borane systems mentioned above. The formation of the dehydrogenated product **MBC–P** is predicted to occur after the cleavage of N–H and B–H bonds leading to a *δ* B–N bond in **MBC–P** that is shorter (*r*B–N = 138.9 pm) than in the reactant **MBC** (*r*B–N = 164.4 pm).



Figure 4: Energy profile for the dehydrogenation of **MBC** without (*via* **MBCTS1**) and with (*via* **MBCTS2**) the presence of BH3 at 298.15 K at the CBS–QB3 level. Relative energies are given in kJ/mol.

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Figure 5: The lowest-energy ground-state structure of the dehydrogenated form of **MBC** (**MBC–P)** showing atom numbering.

Table 5: Bond lengths involved in the dehydrogenation reaction predicted at CBS– QB3 level of theory for **MBC**, **MBCTS1**, **MBCTS2** and **MBC–P**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Distance / pm** | **MBC** | **MBCTS1** | **MBCTS2** | **MBC–P** |
| *r*N–H | 102.0 | 141.4 | 152.0 | – |
| *r*B–H | 121.0 | 138.7 | 133.7 | – |
| *r*B–N | 164.4 | 157.9 | 147.4 | 138.9 |
| *r*H…H | – | 97.3 | 90.8 | – |

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Figure 6: The transition-state structure for the dehydrogenation of **MBC** in the absence of BH3 catalyst (**MBCTS1**).

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Figure 7: The optimized structure of the condensation product formed between **MBC** and BH3 catalyst (**MBC**---BH3).

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Figure 8: The transition-state structure for the dehydrogenation of **MBC** in the presence of BH3 catalyst (**MBCTS2**).

The mechanisms discussed above are supported by examining the thermodynamics of the reaction pathway and the stability of the complex based on the enthalpy of dissociation along the B–N coordinate. The strength of the B–N coordinate is essential in understanding the dehydrogenation process to avoid rupture of the B–N bond prior to the release of the hydrogen molecule. Such a bond has a strength equal to the one-third the strength of a covalent bond as described by Haaland.[76] The thermochemical properties, namely the enthalpy (Δ*H*r), Gibbs free energy (Δ*G*r) and entropy (Δ*S*r) of the dehydrogenation reaction as well as the B–NBDE calculated at the CCSD(T)/CBS and CBS–QB3 levels of theory, are shown in Table 6. While experimental B–NBDEs for morpholine borane and other cyclic amine boranes are not available, a theoretical value for piperidine borane (155.2 kJ/mol)[56] obtained using G4(MP2) method suggest a weaker B–N link than in **MBC**. For linear amine boranes including ammonia borane (NH3BH3), experimental and accurate theoretical values have been reported and are reproduced in Table 7. That these values are lower than in **MBC** may indicate that the dative bond in **MBC** is stronger than in the linear systems. The B–NBDE predicted at CBS–QB3 is found to be higher than the barrier to the dehydrogenation reaction both in the absence and the presence of the BH3 catalyst at the same level of theory. This indicates that the hydrogen molecule will be released before dissociation of the adduct regardless of the pathway followed. The hydrogen release reaction is found to be exothermic with the Δ*H*r value suggesting the release of hydrogen molecule will take place in a near to thermoneutral process. The CBS–QB3 value is similar to that of NH3BH3 (–21.3 kJ/mol)[63] which has been found experimentally to dehydrogenate via thermal decomposition under mild conditions.[77] The predicted Δ*G*r andΔ*S*r shows that the dehydrogenation reaction is exergonic, facile, energetically feasible and will proceed spontaneously towards the release of a hydrogen molecule under standard conditions.

Table 6: Thermochemical properties predicted at 298 K at the CCSD(T)/CBS and CBS–QB3 levels of theory. Units in kJ/molexcept for Δ*S*r which is in J/mol/K.

|  |  |  |
| --- | --- | --- |
| **Property** | **CCSD(T)/CBS** | **CBS-QB3** |
| B–NBDE | +180.3 | +174.1 |
| Δ*H*r | –12.5 | –21.8 |
| Δ*G*r | –48.3 | –57.3 |
| Δ*S*r | +120.5 | +119.2 |

Table 7: Literature B–NBDE values for linear amine borane systems. Units in kJ/mol.

|  |  |  |  |
| --- | --- | --- | --- |
| **System** | **Expt.**A | **CCSD(T)/CBS**B | **G2(MP2)**C |
| NH3BH3 | 130.1(10) | 115.9 | 108.8 |
| CH3H2N–BH3 | 146.4(8) | 139.7 | 133.5 |
| (CH3)2HN–BH3 | 152.3(10) | 153.6 | 147.3 |
| (CH3)3N–BH3 | 145.6(5) | 158.2 | 151.5 |

A Ref.[76], B Ref.[63] and C Ref.[78-79]

**Conclusions**

The molecular structure of **MBC** has been reported for the first time using GED and XRD, and the thermochemical pathways and properties investigated using accurate computational methods. The solid-state and gas-phase molecular structures adopt similar conformations. A longer B–N bond length was observed in the gas-phase; a trend usually observed between solid-state and gas-phase structures.80 The hydrogen storage capability of this complex has been demonstrated by studying the uncatalysed and catalysed reaction energy pathways for hydrogen release and the thermochemistry of the dehydrogenation process has been investigated. The dehydrogenation reaction energies show that the reaction is energetically feasible and will proceed towards unimolecular hydrogen release under relatively mild conditions based on the predicted thermochemical properties. However, no hydrogen release was observed in the gas phase experiment at 375 K, implying that higher temperatures are needed. The results presented herein will enable further study of **MBC** and structural modifications to be made to explore the potential for these systems for on-board chemical hydrogen storage applications.

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**Conflicts of Interest**

The authors declare no conflicts of interest.

**Supplementary Information**

The supporting information contains the experimental parameters and observations for the GED data collection, reduction and refinement of **MBC**; least-squares correlation matrix for the GED refinement; single-crystal XRD data collection, solution and refinement information; calculated Cartesian coordinates at different levels of theory for all the molecules involved; energies and corrections for the thermochemical calculations using different computational methods; calculated and GED refined amplitudes of vibration for each atomic pair in **MBC**; refined and calculated geometric parameters for the gas-phase structure of **MBC**; molecular intensity curves for the GED refinement.

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