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A Computational Characterization of Boron-Oxygen Multiple Bonding in HN=CH-CH=CH-NH-BO

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Abstract

Structures, relative energies, and bonding characteristics for various conformers of 3-imino-N-(oxoboryl)prop-1-en-1-amine, HN=CH-CH=CH-NH-BO, and the corresponding borocycle (–HN=CH-CH=CH-NH-B–)O are discussed using results from second-order Møller-Plesset (MP2) perturbation theory with the Dunning-Woon correlation-consistent cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets. These MP2 results are compared to those from computationally-efficient density functional theory (DFT) calculations using the LDA, PBE, TPSS, BLYP, B3LYP, BVP86, OLYP, O3LYP, and PBE1PBE functionals in conjunction with the economical Pople-type 6–311++G(*d,p*) basis set, to evaluate the suitability of these DFT/6–311++G(*d,p*) levels for use with larger boron-containing systems. The effects of an aqueous environment were incorporated into the calculations using COSMO methodology. The calculated boron-oxygen bond lengths, orbital compositions, and bond orders in all the (acyclic) HN=CH-CH=CH-NH-BO conformers were consistent with the presence of a boron-oxygen triple bond, similar to that found in H–B≡O and H₂N–B≡O. The (–HN=CH-CH=CH-NH-B–)O borocycle is predicted to be planar (C_{2v} symmetry) and it is ~30 kcal/mol *lower* in energy than any of the (acyclic) HN=CH-CH=CH-NH-BO conformers; the boron-oxygen bond in this borocycle has significant double bond character, a bonding scheme for which there has been only one experimental structure reported in the literature

Keywords

Boron-Oxygen Bonding; Oxoboranes; Oxoborons; Boronic Acids; Boron-Nitrogen Bonding; Natural Bond Orbitals

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INTRODUCTION

The chemistry of borates rivals those of the silicates and phosphates in terms of variation and complexity¹. Indeed, the importance of boron derivatives in chemistry^{2,3}, biochemistry^{4,5}, medicinal chemistry^{6–10}, and material science^{11–15}, is increasing rapidly and advancing the understanding of boron bonding continues to be an important topic among chemists^{16,17}. The boron-oxygen single bond in tri-coordinated boronic acids (1.35–1.38 Å) and esters (1.31–1.35 Å)³ is quite strong, ~120 kcal/mol³; not surprisingly, single-bond lengths in tetra-coordinated species are significantly longer (1.43–1.47 Å) and there is an associated loss in bond strength (by as much as 12 kcal/mol)³. Compounds containing boron-oxygen double bonds, *i.e.* oxoboranes (R–B=O), have been invoked as reactive intermediates for some time¹⁸, but they have defied most attempts at isolation and characterization^{18–23}; the oxophilicity of boron makes the formation of a B–O–B linkage more facile than formation of a boron-oxygen multiple bond^{16–17}. Recently, however, Vidovic *et al.*²⁴ reported the synthesis of a novel borocycle, LBO→AlCl₃ (where L is a chelating β-diketiminato; {HC(CMe)₂(NC₆F₅)₂}[–]), in which the boron-oxygen bond was stabilized with a Lewis acid (AlCl₃). LBO→AlCl₃ had significant double bond character, *e.g.* single-crystal X-ray diffraction data collected at 153K showed that the boron-oxygen bond length in this borocycle was 1.304(2) Å compared to 1.354(5) to 1.365(4) Å^{25,26} in singly-bonded N₂B–O fragments (diaz- and triaza-boroles). Furthermore, calculations *in vacuo* performed by the same authors at the B3LYP/6–311+G(*d*) computational level on a (–N(C₆F₅)=C(CH₃)–CH=C(CH₃)–N(C₆F₅)–B–)O borocycle (in the absence or in the presence of a AlCl₃ moiety) indicated that the boron-oxygen functionality in this structure was also predominantly doubled-bonded. However, ongoing computational studies of boron compounds have raised concerns regarding the extent to which the popular B3LYP functional using split-valence Pople-type basis sets adequately describes some aspects of boron bonding^{27–30}, suggesting that more rigorous calculations are required to confirm the Vidovic *et al.*²⁴ results.

Our particular interest in oxoboranes stems from the results of our recent computational investigation²⁹ of several (neutral) reaction mechanisms for the protodeboronation (hydrolysis) of BoroGlycine, H₂N–CH₂–B(OH)₂:

and for the 1,2-carbon-to-nitrogen shift of the –B(OH)₂ moiety,

Surprisingly, a species of the form H₃C–NH₂–B(OH)(=O), in which the boron-oxygen double bond was stabilized by a water molecule, proved to be an intermediate in the 1,2-rearrangement mechanism, leading to this study of boron-oxygen multiple bonding.

In this article we report results from a computational investigation of the structures, relative energies, and boron bonding in various acyclic conformers of 3-imino-N-(oxoboryl)prop-1-en-1-amine, HN=CH–CH=CH–NH–BO, and the related borocycle (–HN=CH–CH=CH–NH–B–)O, which has the same cyclic backbone as the structure synthesized by Vidovic *et al.*²⁴. Conformers of HN=CH–CH=CH–NH–BO are expected to involve a boron-oxygen triple bond^{22,31–38}, see Scheme 1A. Such oxoborons (R–B≡O) have been known experimentally for more than 30 years^{19,22,31,37–42}; they are intermediates in the oxidation of solid borons, boranes, and other boron-based materials and release large amounts of energy when used in the synthesis of boron compounds, making them favorable candidates to be employed as propellants in air-breathing combustors and as rocket fuels^{33,43}. Although life-times of these species are only ~100 ms³⁵, several small oxoboranes have been prepared and their bonding characterized in the gas phase and in the solid state; experimental and computational boron–

oxygen distances in such structures are relatively short^{34,41,42,44}, *e.g.* ~ 1.2 Å for H–B $\equiv$ O^{34,42,45}.

On the other hand, the experimental and computational results reported by Vidovic *et al.*²⁴, suggest that the (–NH=CH–CH=CH–NH–B–)O borocycle is more likely to involve a boron-oxygen double bond, see Scheme 1B. Thus, a rigorous computational investigation of the model compounds HN=CH–CH=CH–NH–BO and (–NH=CH–CH=CH–NH–B–)O provides an opportunity to characterize various aspects of boron-oxygen multiple bonding within a consistent molecular framework^{5,46,47}.

COMPUTATIONAL METHODS

Equilibrium geometries for the structures described in this article were obtained using second-order Møller-Plesset (MP2) perturbation theory⁴⁸ with the frozen core (FC) option, which neglects core-electron correlation; the Dunning-Woon correlation-consistent (cc) basis sets, cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ, were employed for the majority of the computations^{49–52}. Frequency analyses were performed analytically to confirm that the optimized structures were local minima on the PES and to correct reaction enthalpies and free energies to 298K. The gas-phase calculations were carried out using the GAUSSIAN 03 suite of programs⁵³. Bonding was analyzed with the aid of natural bond orbitals (NBOs)^{54–57}.

Calculations using MP2 methodology with cc basis sets are not currently practical for investigations of the larger boron derivatives of primary chemical interest. Density functional theory (DFT) with Pople-style basis sets^{58,59} provide an economical alternative, but the reliability of specific functional/basis set combinations for describing the incredibly diverse range¹ of boron chemistry has yet to be fully established^{27–30}. Thus, our MP2/cc results were compared to those from several more computationally-efficient DFT/6–311++G(*d,p*) levels using the following functionals: LDA(SVWN5)⁶⁰; BLYP and B3LYP, which incorporate the dynamical functional of Lee, Yang, and Parr (LYP)⁶¹, coupled with Becke's pure DFT exchange functional (B)⁶²; BVP86 which uses Perdew's 1986 functional^{63,64} with local correlation replaced by that suggested by Vosko *et al.* (VWN)⁶⁰; OLYP⁶⁵ and O3LYP⁶⁶, which were constructed from the novel OPTX exchange functional; PBE1PBE^{67,68}, which makes use of the one-parameter generalized-gradient approximation (GGA) PBE functional⁶⁹ with a 25% exchange and 75% correlation weighting; and TPSS, the non-empirical meta-generalized gradient approximation (MGGA) functional recently developed by Staroverov, Scuseria, Tao, and Perdew⁷⁰.

Results from continuum solvation models were employed to assess the effects of a bulk aqueous environment on the gas-phase results⁷¹; such continuum models only provide a description of long-range interactions and have significant limitations in describing protic solvents^{72,73}. Thus, in some cases, explicit water molecules were used to provide a description of the short-range/site-specific effects of an aqueous environment. The conductor-like screening model (COSMO), pioneered by Klamt and coworkers^{74–77}, was employed for the continuum calculations in an aqueous medium using the PQS *Ab Initio* Program Package 3.2 on a PQS Quantum Cube⁷⁸; we employed the default settings in the COSMO module of this software which were specifically tailored to COSMO theory^{76,77} and optimized for the BVP86 functional, *i.e.* the BP86 functional^{63,64} in which local correlation was replaced by VWN⁶⁰, using the svp- and tzvp (Ahlrichs) basis sets^{79,80}. These COSMO results were also compared to the corresponding gas-phase results using natural resonance theory (NRT)^{54–57}.

RESULTS AND DISCUSSION

Since no experimental data are currently available for any conformers of $\text{HN}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ or for $(-\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{B}-)\text{O}$, we initially considered $\text{H}-\text{BO}$ ($\text{C}_{\infty\text{h}}$) and $\text{H}_2\text{N}-\text{BO}$ (C_s) at a variety of computational levels to establish “baseline” structural and bonding parameters.

A.1 H-BO AND $\text{H}_2\text{N}-\text{BO}$

A significant amount of experimental^{22,31–38,42} and computational data^{33,45,81–87} have been reported in the literature for hydroboron monoxide, $\text{H}-\text{BO}$, an intermediate/by-product of a variety of reactions involving boron compounds⁸⁸. Calculated bond lengths of $\text{H}-\text{BO}$ at the MP2(FC)/cc-pVDZ, MP2(FC)/aug-cc-pVDZ, and MP2(FC)/cc-pVTZ levels are shown in Figure 1, and vibrational frequencies at the MP2(FC)/aug-cc-pVDZ level are listed in Table 1S of the Supplementary Materials. Structural parameters at a variety of more-rigorous computational levels are given in Table 2S (including selected results that incorporate core-electron correlation (FULL)^{53,89,90}, which has virtually no effect on the calculated geometrical parameters); the analogous structural parameters at several DFT/6–311++G(*d,p*) levels are shown in Table 3S. The calculated boron-oxygen bond lengths, 1.218, 1.222, and 1.214 Å at the MP2(FC)/cc-pVDZ, MP2(FC)/aug-cc-pVDZ, and MP2(FC)/cc-pVTZ levels respectively, all overestimate this length compared to that obtained from microwave spectroscopy, 1.2007 ± 0.0001 Å^{34,41,42,44}; indeed, as shown by DeYonker *et al.*⁴⁵, quite sophisticated computational methodology and large basis sets are required to systematically approach the microwave result. NBOs^{54–57} for $\text{H}-\text{BO}$ at the MP2/cc-pVDZ, MP2/aug-cc-pVDZ, and MP2/cc-pVTZ levels consistently showed the presence of one σ - and two π -boron-oxygen bonding orbitals. NRT^{54–57} calculations with the BVP86 functional using the tzvp (svp) basis sets^{60,63,64,79,80} found the boron-oxygen bond order to be ~ 3.00 in $\text{H}-\text{BO}$, consistent with the presence of a $\text{B}\equiv\text{O}$ bond; the NRT-derived covalent/ionic contributions to the total bond order were 1.24/1.76 at the BVP86/tzvp level; the Löwdin bond order^{91–93} for the boron-oxygen bond in $\text{H}-\text{BO}$ was also calculated and found to be slightly lower, 2.80(2.86), at the BVP86/tzvp(svp) levels, see Table 4S. We also list in Table 4S selected covalent bond orders derived from the atomic overlap matrix (AOM) using the Bader⁹⁴ atoms-in-molecules (AIM) approach to the analysis of electron density^{95–97}.

One measure of the energy content stored in the boron-oxygen triple bond of $\text{R}-\text{B}\equiv\text{O}$ monomers can be obtained from the thermochemical parameters for its trimerization to the heteroaromatic ring ($\text{R}_3\text{B}_3\text{O}_3$) boroxine structure^{35,98–100}. The calculated values of ΔH^0_{298} for the conversion of hydroboron monoxide to $\text{H}_3\text{B}_3\text{O}_3$ ($\text{D}_{3\text{h}}$) are extremely exothermic, -91.1 and -93.2 kcal/mol in *vacuo* at the MP2(FC)/cc-pVDZ and MP2(FC)/aug-cc-pVDZ levels respectively. The calculated boron-oxygen bond lengths in this boroxine are all the same, *e.g.* 1.388 Å at the MP2(FC)/cc-pVDZ level and 1.394 Å at the MP2(FC)/aug-cc-pVDZ level, nearly 0.2 Å longer than the corresponding values in $\text{H}-\text{B}\equiv\text{O}$. The calculated NRT BVP86/svp boron-oxygen bond order in $\text{H}_3\text{B}_3\text{O}_3$ was 1.46 (0.45/1.01), only about 50% of the corresponding value in $\text{H}-\text{B}\equiv\text{O}$, suggestive of significant electron delocalization^{91,98}; the Löwdin bond order was 1.45 at this level, in good agreement with the NRT value, see Table 4S.

In COSMO aqueous media^{76,77} at the BVP86/tzvp level the boron-oxygen bond length of $\text{H}-\text{B}\equiv\text{O}$ increased from the corresponding gas-phase value, but only by ~ 0.005 Å; the boron-oxygen bond order, 3.00 (1.16/1.84), remained essentially the same. Thus, there appears to be relatively little difference in the geometrical structure or in the bonding of $\text{H}-\text{B}\equiv\text{O}$ as a result of any long-range effects of bulk solvation. The calculated values of ΔH^0_{298} for the conversion of hydroboron monoxide to boroxine in COSMO aqueous media at the BVP86/tzvp level was -92.0 kcal/mol compared to -99.3 kcal/mol in *vacuo* at this level. To assess short-range/site-

specific effects of an aqueous environment, we microsolvated the optimized MP2(FC)/cc-pVDZ gas-phase structure of $\text{H}-\text{B}\equiv\text{O}$ with a few explicit water molecules initially positioned in the vicinity of the $\text{B}\equiv\text{O}$ moiety. Although an exhaustive search of all possible conformers of these complexes was not practical at this level, several distinct stable structures were located for 2- and 3-water cases. The lowest-energy forms we found in these hydrated complexes involved an oxygen atom of one of the water molecules effectively bound to the boron atom in $\text{H}-\text{BO}$; the calculated $\text{B}-\text{O}_w$ distance was 1.68(1.67) Å, the $\text{B}-\text{O}$ distance was 1.26(1.27) Å, and the HBO angle was $140.4^\circ(138.5^\circ)$ for the 2(3)-water complexes, see Figure 1S in the Supplementary Materials; thus, there is a significant change from the linear gas-phase geometry of $\text{H}-\text{B}\equiv\text{O}$ on microsolvation. As would be expected, the calculated values of ΔH_{298}^0 for the formation of the lowest-energy 2(3)-water $\text{H}-\text{BO}$ complexes were substantially exothermic, $-18.8(-31.6)$ kcal/mol.

Since the borocycle described by Vidovic *et al.*²⁴, and the model (acyclic) $\text{HN}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ and (cyclic) $(-\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{B}-)\text{O}$ structures, all involve boron–nitrogen bonds, in addition to boron–oxygen bonds, we also geometry optimized aminoboron monoxide, $\text{H}_2\text{N}-\text{BO}$ ⁵, to assess the effect of a proximal boron–nitrogen bond on the boron–oxygen structural and bonding parameters. To the authors' knowledge, no experimental synthesis, isolation, or characterization of $\text{H}_2\text{N}-\text{BO}$, nor any rigorous computational studies of this small molecule, have been reported. The calculated boron–oxygen separation in $\text{H}_2\text{N}-\text{BO}$ was ~ 0.01 Å longer than it was in $\text{H}-\text{B}\equiv\text{O}$ at the MP2(FC)/(cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ) computational levels, see Figure 1; selected structural parameters for $\text{H}_2\text{N}-\text{BO}$ at a variety of DFT/6-311++G(*d,p*) computational levels are listed in Table 3S and show similar increases for the boron–oxygen distance relative to the corresponding values for $\text{H}-\text{B}\equiv\text{O}$. The NBOs of $\text{H}_2\text{N}-\text{BO}$ still involve one σ - and two π -bonds at all the MP2(FC)/cc levels included in this investigation. The NRT boron–oxygen bond order in $\text{H}_2\text{N}-\text{BO}$, 2.90 (1.19/1.71) at the BVP86/tzvp level, was only $\sim 3\%$ lower than the corresponding value in $\text{H}-\text{B}\equiv\text{O}$; the corresponding Löwdin bond order, 2.61, was $\sim 7\%$ lower than that in $\text{H}-\text{B}\equiv\text{O}$. Furthermore, the weighting of the resonance structure of the form $\text{H}_2\text{N}=\text{B}=\text{O}$, associated with the interaction of the nitrogen lone pair orbital and an antibonding boron–oxygen orbital, was only $\sim 9.2\%$ at this level. Thus, in the gas-phase, the boron–oxygen bond in $\text{H}_2\text{N}-\text{BO}$ appears to be best described as a triple bond.

We also calculated thermodynamic parameters for the trimerization of aminoboron monoxide to the boroxine structure $(\text{H}_2\text{N})_3\text{B}_3\text{O}_3$ (D_{3h})³⁵; the calculated values of ΔH_{298}^0 in the gas phase were -134.7 , -130.2 and -125.3 kcal/mol at the MP2(FC)/cc-pVDZ, MP2(FC)/aug-cc-pVDZ, and BVP86/tzvp computational levels respectively, significantly more exothermic than that for the analogous trimerization of hydroboron monoxide. The boron–oxygen bond lengths in the product boroxine structure were all the same, 1.396 Å at the MP2(FC)/cc-pVDZ level and 1.400 Å at the MP2(FC)/aug-cc-pVDZ level, slightly longer than the corresponding values in $\text{H}_3\text{B}_3\text{O}_3$, but indicative of significant electron delocalization^{98–103}; the corresponding boron–nitrogen bond lengths were 1.409 and 1.413 Å, respectively.

As might be expected, in the COSMO aqueous media model^{76,77}, the calculated boron–oxygen bond length in $\text{H}_2\text{N}-\text{BO}$ increased, but only by ~ 0.01 Å at the BVP86/tzvp level compared to the analogous value in *vacuo*; the resulting NRT boron–oxygen bond order, 2.55 (0.98/1.57), however, suggests that in this aqueous model the boron–oxygen bonding in $\text{H}_2\text{N}-\text{BO}$ is best described as intermediate between a double and triple bond; indeed, the NRT weighting of the $\text{H}_2\text{N}=\text{B}=\text{O}$ bonded resonance structure, 41.7%, was more than 4-times greater than the corresponding weighting in *vacuo*. Microsolvation of the gas-phase structure of $\text{H}_2\text{N}-\text{BO}$ with a few water molecules positioned at various points around the boron–oxygen functional group, followed by re-optimization of the complex, often resulted in the corresponding amino boronic

acid, $\text{H}_2\text{N}-\text{B}(\text{OH})_2$, hydrogen-bonded to the remaining water molecules. The hydration reaction:

is highly exothermic in *vacuo*, e.g. ΔH^0_{298} is -44.2 , -41.7 , -46.3 , and -43.0 kcal/mol at the MP2(FC)/cc-pVDZ, MP2(FC)/aug-cc-pVDZ, MP2(FC)/cc-pVTZ, and BVP86/tzvp levels respectively; in COSMO aqueous media at the BVP86/tzvp level, ΔH^0_{298} is -34.7 kcal/mol, ~ 8 kcal/mol *less* negative than the corresponding value in *vacuo*. We also located the 4-membered cyclic transition state for this hydrolysis reaction in *vacuo*, and the value of $\Delta\text{H}^\ddagger$ was only $+4.8$ kcal/mol relative to the separated reactants at the MP2(FC)/cc-pVDZ level. The corresponding value of $\Delta\text{H}^\ddagger$ at the BVP86/tzvp level was predicted to be slightly lower, $+2.2$ kcal/mol, whereas in COSMO aqueous media $\Delta\text{H}^\ddagger$ was found to be slightly higher, $+5.5$ kcal/mol. The calculated values of ΔH^0_{298} for the trimerization of $\text{H}_2\text{N}-\text{B}\equiv\text{O}$ to the corresponding boroxine structure in this COSMO aqueous medium model was -103.0 kcal/mol compared to -125.3 kcal/mol in *vacuo*.

The boron-nitrogen bond length in $\text{H}_2\text{N}-\text{BO}$ was calculated to be 1.41 , 1.40 , and 1.39 Å in *vacuo* at the MP2/cc-pVDZ, MP2/aug-cc-pVDZ, and MP2/cc-pVTZ levels respectively, see Figure 1; the NRT bond order at the BVP86/tzvp level was 1.10 ($0.53/0.59$), generally consistent with the presence of a boron-nitrogen single bond with $\sim 10\%$ double-bond character. The calculated B–N distance *decreased* in COSMO aqueous medium by ~ 0.05 Å at the BVP86/tzvp level and the NRT bond order *increased* to 1.45 ($0.61/0.84$). These findings suggest that the boron-nitrogen bond in this model media is most appropriately described as intermediate between a single and double bond.

A.2 (Acyclic) $\text{HN}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ Conformers

With the above reference data on $\text{H}-\text{BO}$ and NH_2-BO in hand, an extensive conformational search of the (acyclic) $\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ potential energy surface (PES) at the MP2/cc-pVDZ level was performed. A variety of conformers with different *cis/trans* arrangements about the heavy-atom backbone were located; these conformers typically differed in energy among each other by less than ~ 5 kcal/mol. Two of these conformers, **1a** and **1b**, are shown in Figure 2: **1a** (TTT) (C_s) is the lowest-energy acyclic structure we found, whereas conformer **1b** (CCT) (C_s), which is ~ 3 kcal/mol higher in energy than **1a**, see Table 1, has a more “cyclic-like” structure but the terminal nitrogen atom was intentionally oriented to eliminate any possibility of an *intramolecular* boron-nitrogen dative bonding interaction. Infrared vibrational frequencies of **1a** and **1b** at the MP2(FC)/aug-cc-pVDZ level are listed in Table 1S of the Supplementary Materials. Calculated *xyz*-coordinates for a variety of $\text{HN}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ conformers are given in Table 5S of the Supplementary Materials.

The calculated boron-oxygen distances for **1a** in *vacuo*, 1.226 , 1.231 , and 1.223 Å at the MP2(FC)/cc-pVDZ, MP2(FC)/aug-cc-pVDZ, and MP2(FC)/cc-pVTZ levels respectively, see Figure 2, are nearly the same as those in $\text{H}_2\text{N}-\text{B}\equiv\text{O}$ at the corresponding computational levels, see Figure 1. An examination of the NBOs in **1a** at the MP2(FC)/cc-pVDZ and MP2(FC)/aug-cc-pVDZ levels confirmed the existence of a boron-oxygen σ -bonding orbital and predicted a pair of π -bonding orbitals, similar to what was found in both $\text{H}-\text{B}\equiv\text{O}$ and $\text{H}_2\text{N}-\text{B}\equiv\text{O}$. The NRT (BVP86/tzvp) bond order for **1a**, 2.91 ($1.21/1.70$), was almost identical to that for $\text{H}_2\text{N}-\text{B}\equiv\text{O}$, 2.90 ($1.19/1.71$) and the corresponding Löwdin bond order, 2.63 , was nearly the same as in $\text{H}_2\text{N}-\text{B}\equiv\text{O}$, 2.61 , see Table 4S. Furthermore, the weighting of the $\text{B}\equiv\text{O}$ bonded resonance structure was $\sim 62.5\%$ compared to only $\sim 8.4\%$ for the $\text{B}=\text{O}$ bonded structure at the BVP86/tzvp level. Thus, the boron-oxygen bond in **1a** is best described as a triple bond in *vacuo*.

Thermodynamic parameters for the conversion of **1a** to the corresponding $(\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH})_3\text{B}_3\text{O}_3$ boroxine structure⁴² were also computed; the calculated value of ΔH^0_{298} was

−141.1 kcal/mol at the MP2(FC)/cc-pVDZ computational level compared to −134.7 kcal/mol for the analogous conversion of $\text{NH}_2\text{-BO}$.

In the context of the COSMO BPV86/tzvp aqueous medium model, the characteristics of the boron–oxygen bonding in all the (acyclic) HN=CH-CH=CH-NH-BO derivatives that we investigated were similar to those we observed for $\text{H}_2\text{N-BO}$, *e.g.* the boron–oxygen distance in **1a** increased slightly, by ~ 0.007 Å compared to its value in *vacuo*, and the NRT bond order, 2.63 (1.03/1.60), was lower than its value in *vacuo*, 2.91 (1.21/1.70), as was the corresponding Löwdin bond order, 2.55 compared to 2.63. Thus, the boron–oxygen bonding of NH=CH-CH=CH-NH-BO (**1a**) in a COSMO aqueous media model appears to be intermediate between a double and triple bond.

Short-range/site-specific effects of an aqueous environment on the structure of NH=CH-CH=CH-NH-BO (**1a**) were also investigated using a few explicit water molecules initially positioned in the vicinity of the boron–oxygen moiety of the optimized gas-phase MP2(FC)/cc-pVDZ structure. An exhaustive search of all possible conformers of these complexes was obviously not possible, but a variety of different initial arrangements of the water molecules were considered; of course, this does not ensure that we obtained the global minimum on the appropriate PES. As was noted above for $\text{H}_2\text{N-B}\equiv\text{O}$, in some instances these hydrated adducts of NH=CH-CH=CH-NH-BO (**1a**) (in *vacuo*, as well as in COSMO aqueous media) converted to the corresponding boronic acid during the re-optimization; in other adducts the NH=CH-CH=CH-NH-BO structure remained intact, although in these conformers the boron–oxygen bond length was relatively long, ~ 1.28 Å. Indeed, the hydration reaction, $\text{HN=CH-CH=CH-NH-BO(1a)+H}_2\text{O} \rightarrow \text{HN=CH-CH=CH-NH-B(OH)}_2$,

was calculated to be highly exothermic, *e.g.* ΔH_0^{298} was −49.4 and −46.4 kcal/mol at the MP2(FC)/cc-pVDZ and MP2(FC)/aug-cc-pVDZ levels respectively, some 5 kcal/mol *more* exothermic than the analogous reaction for $\text{H}_2\text{N-B}\equiv\text{O}$. We also located the transition state for this hydration reaction in *vacuo*; the value of $\Delta H^\ddagger$ for the formation of the resulting four-membered ring structure was only +1.8 kcal/mol above the separated reactants compared to +4.8 kcal/mol for $\text{H}_2\text{N-B}\equiv\text{O}$.

The boron–nitrogen bonding in **1a** is also similar to that in $\text{H}_2\text{N-BO}$: the compositions of the boron–nitrogen NBOs for NH=CH-CH=CH-NH-BO (**1a**) and $\text{H}_2\text{N-BO}$ were nearly the same at the computational levels we employed, and the calculated BVP86/tzvp NRT bond order in **1a**, 1.09 (0.49/0.60) was almost identical to that in $\text{H}_2\text{N-BO}$, 1.10 (0.51/0.59). The boron–nitrogen bond order for NH=CH-CH=CH-NH-BO (**1a**) in a COSMO BPV86/tzvp aqueous medium was 1.34 (0.55/0.79), attesting to the increased importance of a N=B=O resonance structure in such an environment.

A.3 (−NH=CH−CH=CH−NH−B−)O Borocycle

The (−NH=CH−CH=CH−NH−B−)O borocycle, **1c**, see Figure 2, was ~ 30 kcal/mol lower in energy than any of the acyclic conformers of HN=CH-CH=CH-NH-BO we found at the MP2/cc-pVDZ, MP2/aug-cc-pVDZ, and MP2/cc-pVT levels, see Table 1; infrared frequencies of **1c**, calculated at the MP2/aug-cc-pVDZ level, are listed in Table 1S of the Supplementary Materials. The transition state that connects the borocycle **1c** and the acyclic conformer **1b** of HN=CH-CH=CH-NH-BO was also located, see Figure 2S of the Supplementary Materials; it was 40.5 and 41.0 kcal/mol higher in energy than **1c** at the MP2/cc-pVDZ and MP2/aug-cc-pVDZ levels respectively. The calculated boron–oxygen separation in the borocycle **1c**, 1.266, 1.277, and 1.265 Å at the MP2(FC)/cc-pVDZ, MP2(FC)/aug-cc-pVDZ, and MP2(FC)/cc-pVTZ levels respectively, is ~ 0.04 Å *longer* than it is in the acyclic HN=CH-CH=CH-NH-BO derivatives at these levels. An examination of the NBOs in **1c** at the MP2(FC)/cc-pVDZ and MP2(FC)/aug-cc-pVDZ levels confirms the existence of a boron–oxygen σ -bonding orbital

and one π -bonding orbital. The NRT boron-oxygen bond order for **1c** at the BVP86/tzvp level, 2.28 (0.95/1.33), is significantly lower than the corresponding value for the acyclic conformer, **1a**, 2.91 (1.21/1.70) at this level; the Löwdin bond order for **1c** is 2.32, compared to 2.63 for **1a** and 2.61 in $\text{H}_2\text{N}-\text{B}\equiv\text{O}$. Thus, in *vacuo*, it appears reasonable that the boron-oxygen bond in **1c** can be regarded as predominately a double bond.

In the COSMO BPV86/tzvp aqueous medium model, the length of the boron-oxygen bond in **1c** increased by ~ 0.03 Å to 1.297 Å compared to its value in *vacuo*; the corresponding bond order decreased by ~ 0.3 to 1.95 (0.72/1.23); the Löwdin bond order was only 1.50. We also optimized **1c** in the presence of two and three explicit water molecules, initially positioned in the vicinity of the BO moiety; although our computer resources only allowed a limited exploration of these PESs, the resulting B–O_B distances in the re-optimized complexes tended to be relatively long, *e.g.* ~ 1.30 Å at the MP2(FC)/cc-pVDZ level. Thus, the short-range/site-specific effects of explicit water molecules on this borocycle appear to be less dramatic than those we observed in the acyclic derivatives. Nevertheless, these findings suggest that the boron-oxygen bond in **1c** has a significant degree of double bond character in an aqueous environment.

The calculated value of ΔH_{298}^0 for the hydration reaction,
 $(-\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{B}-)\text{O}(\text{1c})+\text{H}_2\text{O} \rightarrow (-\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{B}-)(\text{OH})_2$,

was -32.6 kcal/mol at the MP2(FC)/cc-pVDZ level, much less exothermic than for the hydrolysis of the acyclic structure $\text{HN}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ (**1a**) or for $\text{H}_2\text{N}-\text{B}\equiv\text{O}$, which is a reflection of the stability of the borocycle **1c** compared to that of **1a**. We located the transition state for this hydrolysis; the value of $\Delta H^\ddagger$ was $+7.6$ kcal/mol at the MP2(FC)/cc-pVDZ level, slightly higher than the corresponding values for $\text{H}_2\text{N}-\text{B}\equiv\text{O}$ ($+4.8$ kcal/mol) and $\text{HN}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ (**1a**) ($+1.8$ kcal/mol).

The two B–N bonds in this novel borocycle **1c** have the same length, *i.e.* there is no structural distinction between the “formal” N–B single bond and the N:B dative bond, a reflection of the extent of electron delocalization in this conformer. The boron-nitrogen distances in **1c**, 1.539, 1.534, 1.529, and 1.538 Å at the MP2(FC)/cc-pVDZ, MP2(FC)/aug-cc-pVDZ, MP2(FC)/cc-pVTZ and BPV86/tzvp levels respectively, are ~ 0.13 Å longer than the corresponding boron-nitrogen separation in **1a** and **1b**.

For a more direct comparison with the experimental results of Vidovic *et al.*²⁴, we also geometry-optimized one conformer of the $(-\text{N}(\text{C}_6\text{F}_5)=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{N}(\text{C}_6\text{F}_5)-\text{B}-)\text{O}$ borocycle at the MP2/cc-pVDZ level in *vacuo*, see Figure 3; the computed boron-oxygen bond length, 1.264 Å, was marginally shorter than the corresponding distance in $\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ (**1c**) at this computational level, but significantly shorter than the calculated value at the B3LYP/6-311+G(*d*) level, 1.292 Å, and even shorter than the experimental X-ray distance in the crystal structure of $(-\text{N}(\text{C}_6\text{F}_5)=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{N}(\text{C}_6\text{F}_5)-\text{B}-)\text{O} \rightarrow \text{AlCl}_3$, 1.304 (2) Å²⁴. The corresponding boron-oxygen bond length for an acyclic conformer of $\text{N}(\text{C}_6\text{F}_5)=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{N}(\text{C}_6\text{F}_5)-\text{BO}$ that is analogous to conformer **1a** of $\text{HN}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ was 1.226 Å at the MP2/cc-pVDZ level, slightly longer than the corresponding length in $\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ (**1a**), but ~ 0.04 Å shorter than this length in $(-\text{N}(\text{C}_6\text{F}_5)=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{N}(\text{C}_6\text{F}_5)-\text{B}-)\text{O}$; this (acyclic) $\text{N}(\text{C}_6\text{F}_5)=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{N}(\text{C}_6\text{F}_5)-\text{BO}$ conformer was 34.4 kcal/mol higher in energy than that for the analogous borocycle. The NBOs of $(-\text{N}(\text{C}_6\text{F}_5)=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{N}(\text{C}_6\text{F}_5)-\text{B}-)\text{O}$ indicate the presence of one σ - and only one π -boron-oxygen bonding orbital suggesting the presence of a double bond, corroborating the interpretation of Vidovic *et al.*²⁴.

A.4 A Comparison of MP2(FC)/(aug)cc-pVxZ (x = D,T) and DFT/6-311++G(d,p) Results for HN=CH-CH=CH-NH-BO and (-NH=CH-CH=CH-NH-B-)O

Calculated boron-oxygen and boron-hydrogen(nitrogen) bond lengths in H-B≡O, H₂N-B≡O, H₂N-B(OH)₂, HN=CH-CH=CH-NH-B≡O(**1a-b**), and (-NH=CH-CH=CH-NH-B-)O (**1c**) are listed in Table 3S at a variety of DFT/6-311++G(d,p) levels; the Pople-style 6-311++G(d,p) basis set is at the “upper-end” of basis sets that are likely to be employed in studies of larger boron containing compounds in the near future. In this investigation we have performed a limited comparison between the more rigorous MP2(FC) methodology using the (aug)cc-pV(D,T)Z, basis sets and the more economical DFT methodology with the LDA, PBE, TPSS, BLYP, B3LYP, BVP86, OLYP, O3LYP, and PBE1PBE functionals using the 6-311++G(d,p) basis set.

Comparing the calculated MP2/(cc-pVDZ, aug-cc-pVDZ, cc-pVTZ) boron-oxygen bond distances, see Figure 1 and Figure 2, and the corresponding DFT/6-311++G(d,p) distances given in Table 3S, it is evident that there is reasonable agreement among these various methods/basis-sets to within ~0.02 Å. The calculated boron-oxygen bond length in H-B≡O at *both* the B3LYP/6-311++G(d,p) and the PBE1PBE/6-311++G(d,p) levels was in particularly good agreement with the microwave data, see Table 3S. Furthermore, this finding does not appear to be highly basis-set dependent - the boron-oxygen bond lengths calculated using the B3LYP functional with the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets were 1.203, 1.205, and 1.200 Å respectively, and the corresponding PBE1PBE distances were 1.202, 1.204 and 1.199 Å.

Values for a variety of DFT/6-311++G(d,p) energy differences among the acyclic conformers **1a** and **1b** of HN=CH-CH=CH-NH-BO and of the borocycle (-NH=CH-CH=CH-NH-B-)O **1c** are listed in Table 6S of the Supplementary Materials. A comparison of Table 1 and Table 6S shows that there is good agreement between the relative energies of **1a** and **1b** at the various DFT/6-311++G(d,p) and the MP2(FC)/cc levels, *i.e.* conformer **1b** is consistently ~3–4 kcal/mol higher in energy than **1a**. As might be expected, the variation of energy values (corrected to 298K) between the borocycle **1c** and the acyclic conformer **1a** is significantly greater, ranging from 27.8 kcal/mol (B3LYP) to 42.5 kcal/mol (LDA); however, ignoring the LDA value, which includes only local terms in the correlation functional, the variation is significantly less, the highest value is 35.3 kcal/mol (PBE1PBE); the corresponding MP2(FC)/(aug)-cc-pVD(T)Z values range from 29.8 to 32.3 kcal/mol, see Table 1. Thus, to a large extent, these DFT/6-311++G(d,p) energy differences are in quite good agreement with the available MP2(FC)/cc results; unfortunately, no experimental data are currently available for comparison. In view of our previous results involving dative bonding interactions^{27–30} it appears that the PBE1PBE/6-311++G(d,p) computational level is a reasonable, economical alternative to the more-costly MP2(FC)/cc levels for exploring various aspects of boron chemistry.

It is of interest to assess geometrical and energetic results associated with climbing the DFT ladder (“Jacob’s ladder”): LDA→PBE→TPSS¹⁰⁴, using the modest 6-311++G(d,p) basis set. The calculated LDA/6-311++G(d,p) boron-oxygen bond length in H-B≡O, 1.202 Å is in excellent agreement with the experimental microwave value 1.201 Å, as well as with the corresponding B3LYP and PBE1PBE values. The initial LDA→PBE step on the ladder at this computational level results in a boron-oxygen bond length that is ~0.01 Å longer, and nearly the same as the MP2(FC)/6-311++(d,p) length, 1.212 Å. The second step on the DFT ladder is PBE→TPSS; at this step the boron-oxygen bond length changes minimally, see Table 3S. The energy difference between the borocycle **1c** and the acyclic derivative **1b** improves dramatically in going from LDA to PBE compared to the various MP2(FC)/cc differences and most of the DFT/6-311++G(d,p) differences, see Table 1 and Table 6S; the energy change in going from PBE to TPSS is minimal.

CONCLUDING REMARKS

The importance of boron chemistry is increasing rapidly in a variety of fields, and unveiling the intricacies of boron bonding remain an active area of research^{3,17,19,24,26,29,81,82}. In this article we report results from a computational investigation of the boron-oxygen bonding in H-BO and H₂N-BO, as well as in the acyclic conformers of HN=CH-CH=CH-NH-BO (**1a**, **1b**) and in the corresponding borocycle (-NH=CH-CH=CH-NH-B-)O (**1c**); MP2 methodology with the correlation-consistent cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis sets and DFT methodology with the 6-311++G(*d,p*) basis set were employed for the calculations.

Experimentally and/or computationally derived distances between the boron and oxygen atoms, a key parameter in any discussion of bond order¹⁰⁵, the calculated composition of the molecular orbitals at a variety of MP2/cc and DFT/6-311++G(*d,p*) levels, and the computed NRT bond orders at the BVP86/(svp)tzvp-Ahlrichs levels are consistent with the presence of a boron-oxygen triple bond in H-BO, H₂N-BO, and various (acyclic) conformers of HN=CH-CH=CH-NH-BO in *vacuo*. Using the COSMO BVP86/(svp)tzvp models to simulate the long-range effects of an aqueous medium, the boron-oxygen bond in H-BO was still best described as a triple bond, whereas for H₂N-BO and HN=CH-CH=CH-NH-BO(**1a**, **1b**) this bond appears to be more appropriately described as intermediate between a double and triple bond. Incorporating several explicit water molecules in the vicinity of the boron-oxygen bond during the optimization of complexes of H₂N-B=O and HN=CH-CH=CH-NH-BO(**1a**), to account for short-range/site-specific effects on the boron-oxygen bonding, often resulted in the corresponding boronic acid, suggesting that in an aqueous environment the presence of H₂N-B=O or HN=CH-CH=CH-NH-BO(**1a**, **1b**) would be short-lived. The boron-nitrogen bond in H₂N-B=O and HN=CH-CH=CH-NH-B=O(**1a**, **1b**) was predominantly a single bond in *vacuo*, but was predicted to have substantial double bond character by the COSMO BPV86/tzvp aqueous media model.

At all the MP2(FC)/(aug)-cc-pVxZ and DFT/6-311+G(*d,p*) computational levels we employed in this investigation, the (-NH=CH-CH=CH-NH-B-)O borocycle, **1c** (C_{2v} symmetry), was ~30 kcal/mol *lower* in energy than any of the HN=CH-CH=CH-NH-B=O acyclic conformers we found, see Table 1 and Table S5. All indications are that the boron-oxygen bond in this borocycle is predominantly a double bond, in accord with the available experimental results on (-N(C₆F₅)=C(CH₃)-CH=C(CH₃)-N(C₆F₅)-B-)O²⁴. The calculated lengths of the two boron-nitrogen bonds in **1c** and (-N(C₆F₅)=C(CH₃)-CH=C(CH₃)-N(C₆F₅)-B-)O were identical, a measure of the extent of electron delocalization in this conformer.

The hydration reactions,

were calculated to be highly exothermic; the calculated values of ΔH_{298}^0 for **1a** and **1c** were -49.4 and -32.6 kcal/mol respectively at the MP2(FC)/cc-pVDZ level, an indication of the amount of energy stored in the boron-oxygen bond in these compounds. Furthermore, the calculated value of ΔH_{298}^0 for the trimerization reaction of HN=CH-CH=CH-NH-BO(**1a**) to form the ((NH=CH-CH=CH-NH)₃B₃O₃) boroxine structure was -141.1 kcal/mol at the MP2(FC)/cc-pVDZ computational level. These findings help to quantify the high-energy content of BO multiple bonds.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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MP2(FC)/cc-pVDZ
MP2(FC)/aug-cc-pVDZ
MP2(FC)/cc-pVTZ

Figure 1.
Optimized structures of HBO, H₂NBO and H₂NB(OH)₂. (Distances are in Å).

Figure 2. Optimized structures of the acyclic conformers **1a** and **1b** of $\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{BO}$ and the borocycle **1c** ($-\text{NH}=\text{CH}-\text{CH}=\text{CH}-\text{NH}-\text{B}-\text{O}$). (Distances are in Å). (AIM calculations using the MP2/cc-pVDZ density find the expected molecular graph for **1c** (12 attractors, 12 critical points on attractor interaction lines, and 1 ring point.)

MP2(FC)/cc-pVDZ

Figure 3. Optimized structures of the borocycle $(-N(C_6F_5)=C(CH_3)-CH=C(CH_3)-N(C_6F_5)-B-)O$ and the acyclic conformer $N(C_6F_5)=C(CH_3)-CH=C(CH_3)-N(C_6F_5)-BO$ at the MP2/cc-pVDZ computational level.

A **B****Scheme 1.**

Table 1

Relative Energies, E(kcal/mol) (Values Thermally Corrected to 298 K° Are Given in Parentheses) for the Acyclic conformers **1a** (TTT) and **1b** (CCT) of NH=CH-CH=CH-NH-BO and the cyclic conformer **1c** (CCC) of (-NH=CH-CH=CH-NH-B-)O at the MP2(FC)/cc-pVDZ, MP2(FC)/aug-cc-pVDZ, and MP2(FC)/cc-pVTZ Computational Levels.

Level	E(kcal/mol) 1c (CCC)	E(kcal/mol) 1a (TTT)	E(kcal/mol) 1b (CCT)
MP2(FC)/cc-pVDZ	0.0(0.0)	+31.4(+29.8)	+34.8(+33.3)
MP2(FC)/aug-cc-pVDZ	0.0(0.0)	+32.6(+31.1)	+35.3(+33.8)
MP2(FC)/cc-pVTZ	0.0 (0.0)	+33.9(+32.3)	+36.9(+35.4)