

## Hybrid Meta-Generalized Gradient Functional Modeling of Boron–Nitrogen Coordinate Covalent Bonds

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Received May 5, 2008

**Abstract:** Truhlar's new generation of hybrid meta-generalized gradient functionals has been evaluated in modeling the binding enthalpies of substituted B–N coordinate covalent bonds. The short-range exchange correlation (XC) energy of coordinate covalent bonding coupled with the medium-range XC energy of noncovalent interactions results in a particularly difficult case for density functional theory (DFT). In this study, M06, M06–2X, M05, M05–2X, MPWB1K, and MPW1B95 with the 6–311++G(3df,2p) basis set have been used to evaluate four methylated ammonia trimethylboranes,  $(\text{CH}_3)_3\text{B}-\text{N}(\text{CH}_3)_n\text{H}_{3-n}$  ( $n = 0$  to 3), along with  $\text{H}_3\text{B}-\text{NH}_3$ . The predicted binding enthalpies from the new functionals have been compared to experiment as well as previous DFT (B3LYP, MPW1K) and ab initio (HF, MP2, QCISD, and QCISD(T)) results. Previously, only MP2, QCISD, and QCISD(T) were found to model the experimental energetic trend accurately. The mean absolute deviation (MAD) from experimental binding enthalpies for M06–2X and M05–2X is 0.3 and 1.6 kcal/mol, respectively. M06–2X yields a lower MAD than more expensive ab initio methods (MP2 = 1.9 kcal/mol and QCISD = 2.3 kcal/mol) and a comparable MAD to QCISD(T) (MAD = 0.4 kcal/mol). M06–2X is shown to provide a balanced account of the short- and medium-range XC energies necessary to describe the binding enthalpy of coordinate covalent bonds accurately in sterically congested molecular systems.

### Introduction

Kohn–Sham density functional theory (DFT)<sup>1</sup> has become a well-established tool in the computational chemistry community. Despite broad applicability across many areas of chemistry, DFT computations have resulted in a number of limitations involving unreliable barrier heights, noncovalent interactions, and aspects of transition metal chemistry, as recently reviewed by Zhao and Truhlar<sup>2</sup> and Sousa et al.<sup>3</sup> It is known that DFT accuracy issues originate from the approximation of the exchange–correlation (XC) functional within the Kohn–Sham formalism.<sup>1,3</sup> Current DFT implementations, such as the local spin density approximation (LSDA),<sup>1,4</sup> generalized gradient approximation (GGA),<sup>5–10</sup> meta-GGA (M-GGA),<sup>11,12</sup> hybrid-GGA (H-GGA),<sup>5,9,11,13,14</sup> and hybrid meta-GGA (HM-GGA),<sup>15–17</sup> treat the XC func-

tional differently. LSDA assumes that the XC energy at any point in space depends only on the spin density at that specific spatial region. GGA improves upon LSDA by considering the gradient of the density along with the spin density. Further improvements of GGA include the spin-dependent electronic kinetic energy (M-GGA) and a certain percentage of Hartree–Fock exchange (H-GGA). Finally, the HM-GGA incorporates both approximations from M-GGA and H-GGA.

A known case reflecting a challenge for DFT computations<sup>18</sup> is presented by the experimental binding enthalpies of four methylated ammonia borane trimethylboranes,  $(\text{CH}_3)_3\text{B}-\text{N}(\text{CH}_3)_n\text{H}_{3-n}$  ( $n = 0$  to 3) and  $\text{H}_3\text{B}-\text{NH}_3$ .<sup>19</sup> The B–N coordinate covalent bond strength has been observed by experiment to increase for each methyl group added to the nitrogen atom ( $n = 0$  to 2) until the third methyl group ( $n = 3$ ), in which the strength decreases to that of the one

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methyl case.<sup>19</sup> The experimental uncertainty was determined to be less than or equal to 0.3 kcal/mol.<sup>19</sup> Although an experimental binding enthalpy for ammonia borane is not known, estimates from experimental data<sup>20,21</sup> and ab initio methods<sup>18,22,23</sup> report that the ammonia borane B–N coordinate covalent bond is stronger than the methyl substituted ammonia trimethylboranes considered here. The relative experimental binding enthalpies across the five adducts is difficult to model by computational methods accurately, due to the critical mix of short- and medium-range XC energy necessary to describe the coordinate covalent bond and the nonbond interactions with increasing alkyl substitution.

Recently, we have reported the binding enthalpies for  $(\text{CH}_3)_3\text{B}-\text{N}(\text{CH}_3)_n\text{H}_{3-n}$  ( $n = 0$  to 3) and  $\text{H}_3\text{B}-\text{NH}_3$  employing HF, B3LYP, MPW1K, MP2, QCISD, and QCISD(T) with the 6-311++G(3df,2p) basis set.<sup>18</sup> Only MP2, QCISD, and QCISD(T) were found to model the experimental trend in binding enthalpies accurately. Others have also reported deficiencies with commonly employed functionals when modeling coordinate covalent bonds.<sup>22,23</sup> For example, B3LYP binding energies and structures resulted with increasing error, as methyl groups were systematically added to the donor and acceptor atoms of ammonia borane.<sup>22</sup> Similarly, B3LYP computational results were unable to predict the energetics of the B–N coordinate covalent bond within borate systems.<sup>23</sup> However, MP2 predicted trends in binding enthalpies are consistent with experiment.<sup>22</sup> In a systematic analysis of ammonia borane and  $(\text{CH}_3)_3\text{B}-\text{N}(\text{CH}_3)_n\text{H}_{3-n}$ , quantitative accuracy (MAD = 0.4 kcal/mol) of binding enthalpies was determined with QCISD(T)/6-311++G(3df,2p) single point energy evaluations on MP2/6-311++G(3df,2p) optimized structures. (Reference 18 concentrated on only the four alkyl substituted adducts. The MAD computed in that paper omitted ammonia borane, and resulted in a QCISD(T) MAD of 0.5 and MP2 MAD of 2.2 kcal/mol. Statistical analysis of binding enthalpies including ammonia borane is given in the present work.) The electronic energy was corrected for BSSE, basis set limit, and appropriate thermal factors.<sup>18</sup> However, this strategy is resource intensive and limited to small systems. MP2/6-311++G(3df,2p) delivers semiquantitative results (MAD = 1.9 kcal/mol), maintaining the qualitative trend, when corrected as given above. Although MP2 is not as resource intensive as QCISD(T), MP2 remains an impractical and inefficient choice for large chemical systems. It would be beneficial to identify improved DFT functionals, so larger chemical assemblies possessing coordinate covalent chemical bonding may be investigated with structural and thermodynamic accuracy.

Truhlar and co-workers have developed a new generation of DFT methods that have shown significant accuracy improvements when considering thermochemistry, kinetics, noncovalent interactions, excited states, and treatment of transition metals.<sup>2</sup> Of the many functionals parameterized and designed by Truhlar and co-workers, the present work considers the HM-GGA functionals, M06–2X, M06, M05–2X, M05, MPW1B95, and MPWB1K. Before the existence of the Minnesota functionals (M06–2X, M06, M05–2X, and M05), MPWB1K and MPW1B95 were

among the best for analyzing noncovalent interactions dominated by medium-range XC energy.<sup>16,24</sup> M05–2X and M05 were initially recommended when a combination of nonmetallic thermochemistry, kinetics, and noncovalent interactions were investigated,<sup>15,25</sup> while M05 was suggested for exploring organometallic and inorganometallic thermochemistry.<sup>15,25</sup> Subsequently, M06–2X and M06 have been recommended for a wide range of chemical phenomena.<sup>17</sup> A recent review by Truhlar assessed the accuracy of many functionals against 496 data values within 32 databases including thermochemistry, barrier heights, noncovalent interactions, electronic spectroscopy, and structural data.<sup>2</sup> Finally, M06–2X, M05–2X, and M06 were suggested for systems where main-group thermochemistry, kinetics, and noncovalent interactions are important.<sup>2</sup> M06 was recommended specifically for transition metal thermochemistry involving both reactive organic and transition metal bonds.<sup>2</sup>

Proper description of short-range XC energy of coordinate covalent bonding coupled with the medium-range XC energy of noncovalent substituent interactions is important in many fields of chemistry. Since the Lewis acid adducts explored within the present work possess short- and medium-range XC, the M06, M06–2X, M05, M05–2X, MPW1B95, and MPWB1K functionals have been employed to explore the thermochemistry and electronics within the B–N coordinate covalent bond and alkyl substituted cases. The  $(\text{CH}_3)_3\text{B}-\text{N}(\text{CH}_3)_n\text{H}_{3-n}$  complexes and ammonia borane have been chosen for analysis due to the reported difficulty in modeling the energetic character of the corresponding B–N coordinate covalent bonds, where only computationally intense ab initio methods (MP2, QCISD, and QCISD(T)) have been able to model the experimental trend of binding enthalpies accurately.<sup>18</sup> Besides interest in the fundamental treatment of coordinate covalent bonds,<sup>20,26</sup> the new generation of density functionals may provide improved structural and energetic description of coordinate covalent bonds that occur in larger biochemical systems<sup>27,28</sup> and new materials.<sup>29,30</sup>

## Computational Details

All electronic structure calculations were carried out with G03<sup>31</sup> and NWChem 5.1<sup>32</sup> using the computational resources at the Center for Computational Sciences at Duquesne University. NWChem 5.1 was utilized for M06 and M06–2X computations. Full electronic structure optimizations on  $\text{H}_3\text{B}-\text{NH}_3$  and  $(\text{CH}_3)_3\text{B}-\text{N}(\text{CH}_3)_n\text{H}_{3-n}$  ( $n = 0$  to 3) were performed with HM-GGA DFT, specifically MPW1B95,<sup>16</sup> MPWB1K,<sup>16</sup> M05–2X,<sup>15</sup> M05,<sup>15,25</sup> M06–2X,<sup>17</sup> and M06.<sup>17</sup> The design and parameterization of these functionals have been discussed in great detail within the corresponding references and recently reviewed.<sup>2</sup> The computational protocol within the present analysis is the same as reported previously,<sup>18</sup> except for the implementation of NWChem and the consideration of Radom and co-worker's updated scaling factors. Specifically, it is known that Gaussian03 and NWChem 5.1 utilize 5 *d* and 7 *d* (pure) and 6 *d* and 10 *f* (Cartesian) angular momentum basis functions as the default, respectively. The SPHERICAL keyword has been implemented within NWChem to utilize 5 *d* and 7 *f* functions. In addition, Radom and co-workers recently reported new scaling factors for B3LYP/

**Table 1.** Predicted and Experimental Binding Enthalpies,  $\Delta H_T$  (kcal/mol)<sup>a</sup>

	BH <sub>3</sub> –NH <sub>3</sub>	B(CH <sub>3</sub> ) <sub>3</sub> –NH <sub>3</sub>	B(CH <sub>3</sub> ) <sub>3</sub> –NH <sub>2</sub> CH <sub>3</sub>	B(CH <sub>3</sub> ) <sub>3</sub> –NH(CH <sub>3</sub> ) <sub>2</sub>	B(CH <sub>3</sub> ) <sub>3</sub> –N(CH <sub>3</sub> ) <sub>3</sub>	MAD
HF <sup>18</sup>	–16.5	–2.0	–3.5	–1.2	3.6	15.2
M05	–23.2	–6.8	–9.0	–7.3	–2.4	9.4
B3LYP <sup>18</sup>	–24.7	–6.8	–8.8	–7.0	–2.4	9.2
MPW1K <sup>18</sup>	–29.2	–11.9	–14.2	–12.9	–9.1	4.4
MPW1B95	–30.0	–12.5	–15.4	–14.9	–12.5	3.1
<b>QCISD/MP2<sup>18</sup></b>	<b>–26.1</b>	<b>–12.6</b>	<b>–13.8</b>	<b>–16.8</b>	<b>–14.7</b>	<b>2.3</b>
<b>M06</b>	<b>–25.3</b>	<b>–10.3</b>	<b>–14.0</b>	<b>–14.5</b>	<b>–12.5</b>	<b>3.9</b>
MPWB1K	–30.3	–13.4	–16.4	–16.1	–13.9	2.3
<b>MP2<sup>18</sup></b>	<b>–28.0</b>	<b>–15.6</b>	<b>–20.1</b>	<b>–21.4</b>	<b>–20.2</b>	<b>1.9</b>
<b>M05–2X</b>	<b>–25.9</b>	<b>–12.2</b>	<b>–16.3</b>	<b>–17.3</b>	<b>–16.1</b>	<b>1.6</b>
<b>QCISD(T)/MP2<sup>18</sup></b>	<b>–27.5</b>	<b>–14.4</b>	<b>–18.6</b>	<b>–19.5</b>	<b>–17.8</b>	<b>0.4</b>
<b>M06–2X</b>	<b>–27.8</b>	<b>–14.2</b>	<b>–18.4</b>	<b>–19.2</b>	<b>–17.8</b>	<b>0.3</b>
experiment <sup>19</sup>	–27.5 ± 0.5 <sup>b</sup>	–13.8 ± 0.3	–17.6 ± 0.2	–19.3 ± 0.3	–17.6 ± 0.2	

<sup>a</sup> BSSE corrections and convergence corrections of 1.5, 1.3, and 1.6 kcal/mol for MP2, QCISD, and QCISD(T), respectively, have been applied according to ref 18. The temperatures are 298 for BH<sub>3</sub>–NH<sub>3</sub> and 373 for (CH<sub>3</sub>)<sub>3</sub>B–N(CH<sub>3</sub>)<sub>n</sub>H<sub>3–n</sub>;  $n = 0$  to 3. The 6–311++G(3df,2p) basis set has been employed with all chemical methods. Chemical methods in boldface indicate that the experimental trend was reproduced. <sup>b</sup> Best estimate predicted by QCISD(T)/aug-cc-pV5Z//MP2/6–311++G(3df,2p), see ref 18.

**Table 2.** Basis Set Superposition Error (kcal/mol)<sup>a</sup>

	BH <sub>3</sub> –NH <sub>3</sub>	B(CH <sub>3</sub> ) <sub>3</sub> –NH <sub>3</sub>	B(CH <sub>3</sub> ) <sub>3</sub> –NH <sub>2</sub> CH <sub>3</sub>	B(CH <sub>3</sub> ) <sub>3</sub> –NH(CH <sub>3</sub> ) <sub>2</sub>	B(CH <sub>3</sub> ) <sub>3</sub> –N(CH <sub>3</sub> ) <sub>3</sub>	average
HF <sup>18</sup>	0.2	0.3	0.3	0.3	0.4	0.3
M05	0.2	0.4	0.3	0.4	0.4	0.4
B3LYP <sup>18</sup>	0.2	0.3	0.3	0.4	0.4	0.3
MPW1K <sup>18</sup>	0.2	0.3	0.4	0.4	0.5	0.4
M06	0.3	0.4	0.5	0.6	0.7	0.5
MPW1B95	0.2	0.3	0.3	0.4	0.5	0.3
MPWB1K	0.2	0.3	0.3	0.3	0.4	0.3
M05–2X	0.2	0.3	0.4	0.5	0.6	0.4
M06–2X	0.2	0.3	0.5	0.5	0.7	0.4

<sup>a</sup> BSSE computed by subtracting the  $\Delta H$  BSSE corrected value from the  $\Delta H$  uncorrected value. The 6–311++G(3df,2p) basis set has been utilized.

6–31G(d) predicted enthalpy corrections.<sup>33</sup> However, the new enthalpy corrections corresponding to  $T = 298$  and 373 K are 1.0004 and 0.9953 (interpolated), yielding negligible differences between predicted binding enthalpies using the newer and older scaling factors. Consequently, the older scaling factors have been used for consistency and comparison with previous HF, B3LYP, MPW1K, MP2, QCISD, and QCISD(T) results.<sup>18</sup>

## Results and Discussion

**Binding Enthalpies of B–N Coordinate Covalent Bonds.** The strength of the coordinate covalent bond has been assessed by predicting the binding enthalpy of each adduct utilizing M06, M06–2X, M05–2X, M05, MPWB1K, and MPW1B95. The results are compared to experimental binding enthalpies reported by Brown and co-workers<sup>19</sup> and previous theoretical values.<sup>18</sup> Previous analysis of HF, B3LYP, MPW1K, MP2, QCISD, and QCISD(T) determined that only ab initio methods were able to replicate the experimental binding enthalpy trend, as shown by Table 1.<sup>18</sup> M06–2X, M06, and M05–2X are the only DFT methods found to replicate the B–N coordinate covalent bond strengthening upon methyl substitution on the donor side ( $n = 0$  to 2) with subsequent weakening as the last methyl group is added ( $n = 3$ ). All methods predict a stronger ammonia borane B–N coordinate covalent bond as compared to the trimethylboranes.

M06 yields the highest MAD (3.9 kcal/mol) out of the functionals able to reproduce the experimental trend and

consistently underestimates the strength of the B–N coordinate covalent bond. M05–2X yields a comparable MAD to MP2 at a much lower computational cost. Formally, MP2 scales as  $N^5$ , while DFT scales as  $N^3$  ( $N$  = number of basis functions).<sup>3</sup> M05–2X and MP2 MADs are 1.6 and 1.9 kcal/mol, respectively; however, MP2 tends to overestimate the strength of the coordinate covalent bond, while M05–2X underestimates it. M06–2X is comparable to QCISD(T), yielding a MAD of 0.3 kcal/mol, 0.1 kcal/mol lower than that of QCISD(T)'s MAD. Thus, M06–2X is a practical and efficient functional suitable for modeling the energetic character of the B–N coordinate covalent bond. In contrast of resources, QCISD(T) scales as  $N^7$  compared to DFT methods which grow as  $N^3$ .<sup>3</sup> Furthermore, M06–2X does not require a convergence correction for the basis set limit, a requirement for QCISD(T) to realign predicted results with experiment, due to the slow convergence of predicted post SCF results on larger molecular systems.<sup>18</sup>

**Basis Set Superposition Error for DFT.** As reported for ammonia borane and methyl substituted ammonia boranes, post SCF methods result in more BSSE than HF and DFT methods, and convergence to the complete basis set limit is much slower.<sup>18</sup> When post SCF methods are corrected for BSSE, the complete basis set limit was not reached with the 6–311++G(3df,2p) basis set. For practicality, residual convergence corrections were added to yield the appropriate binding enthalpies determined using the 6–311++G(3df,2p) basis set. However, HF and DFT methods possessed less



than 0.5 kcal/mol of BSSE, and binding enthalpies were considered converged.

The amount of BSSE for all functionals and HF is displayed in Table 2. M06, M06-2X, M05, M05-2X, MPWB1K, and MPW1B95 have comparable amounts of BSSE when employed with the 6-311++G(3df,2p) basis set to that of the other functionals and HF.

Since HF, B3LYP, and MPW1K yield a converged binding enthalpy at this basis set, it is reasonable to assume that the other functionals, M06, M06-2X, M05, M05-2X, MPWB1K, and MPW1B95, behave similarly. A M06-2X/aug-cc-pVQZ optimization of ammonia borane supports this assumption, where the B-N coordinate covalent bond lengths and BSSE corrected binding enthalpies differ by 0.0008 Å and 0.2 kcal/mol, respectively, as compared to that computed by M06-2X/6-311++G(3df,2p). Consequently, M06-2X is used with the 6-311++G(3df,2p) basis set to deliver a value near convergence with a minimum amount of BSSE without jeopardizing efficiency and practicality.

**M06-2X Origin of Success.** M06-2X, M06, and M05-2X are the only DFT methods found in this study that reproduce the experimental trend in binding enthalpies. Furthermore, only M06-2X and M05-2X yield comparable MADs to QCISD(T) and MP2, respectively. The Minnesota functionals were designed with a balance of kinetic energy density between the exchange and correlation functionals. In contrast, MPWB1K and MPW1B95 incorporate kinetic energy density within the correlation functional only, while B3LYP and MPW1K consider it in neither the exchange nor the correlation functionals. However, this cannot be the only reason for the relative quantitative success of M06-2X and M05-2X, since M05 also incorporates kinetic energy density in both the exchange and correlation functionals and is unable to model the experimental trend. The two main differences between the successful functionals (M06-2X and M05-2X) and M06 involves nearly double the amount of Hartree-Fock exchange (M06-2X and M05-2X) and a different formulation of the functional form (M06-2X). The linear combination of the M05 class functional and VSXC<sup>12,34</sup> (yielding the M06 style) allows both M06 and M06-2X to model the experimental binding enthalpy *trend* accurately; however, doubling the Hartree-Fock exchange allows a more *quantitative* assessment of the B-N coordinate covalent bond by M06-2X compared to M06. The empirical nature of the functional forms associated with M06-2X, M06, M05-2X, and M05, possessing 33, 36, 23, and 23 optimized parameters, respectively, may contribute to the high accuracy as well. However, M05 possesses the same number of optimized parameters as M05-2X and is unable to account for the experimental trend. In contrast, M05-2X is able to reproduce the experimental trend by just doubling the amount of Hartree-Fock exchange but with a higher MAD compared to M06-2X. Consequently, the balance of kinetic energy density in both the exchange and correlation functionals, the higher amount of Hartree-Fock exchange, and the functional forms of the exchange and correlation functionals within the M06 class of functionals are critical in order to model a balance of short- and medium-range XC interactions that

exist within the B-N coordinate covalent bond and steric interactions, respectively.

## Conclusions

The inherent difficulty of modeling the B-N coordinate covalent bond strength within ammonia borane and four methyl substituted trimethylboranes using Truhlar's hybrid meta-generalized gradient functionals (M06-2X, M06, M05-2X, M05, MPWB1K, MPW1B95) has been investigated. Previously, only ab initio methods (MP2, QCISD, and QCISD(T)) have been able to model the experimental trend accurately, with MP2 and QCISD(T) yielding lower MADs than QCISD. Of the new functionals explored, M06-2X, M06, and M05-2X are able to reproduce the experimental trend with MADs of 0.3, 3.9, and 1.6 kcal/mol, respectively. M05-2X and M06-2X yield comparable MADs to that of MP2 (MAD = 1.9 kcal/mol) and QCISD(T) (MAD = 0.4 kcal/mol), respectively. M06-2X is able to model the B-N coordinate covalent bond efficiently and accurately without the residual convergence correction and intense computational resources necessary for MP2, QCISD, and QCISD(T). M06-2X incorporates the proper balance of short-range XC energy necessary to model the electronics within the B-N coordinate covalent chemical bond as well as the medium-range XC energy required by sterically congested environments near the coordinate covalent bond. M06-2X computations result in superior performance, due to the balance of kinetic energy density in the exchange and correlation functionals, the higher amount of Hartree-Fock exchange, and the functional forms of the exchange and correlation functionals. M06-2X/6-311++G(3df,2p) is able to model the electronics of the B-N chemical bond and is a more practical and efficient choice for investigating chemical systems possessing B-N coordinate covalent bonds, where quantitative trends in energetics are necessary.

**Acknowledgment.** This work was funded in part by the NSF and DoD (CHE-0723109, CHE-0649182, CHE-0321147, CHE-0354052, AAB/PSC CHE-030008P), Department of Education (P116Z040100 and P116Z050331), and the Silicon Graphics Inc., James River Technical, Inc., and Gaussian Corporations. The authors acknowledge Dr. Doug Fox (Gaussian) for his expertise, knowledge, and discussions crucial to this study.

**Supporting Information Available:** Full Gaussian and NWChem citation, all optimized structures, frequencies, thermodynamic data, interpolation of scaling factor at 373 K, and BSSE uncorrected binding enthalpies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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CT800210E