A test of density functional theory for dative bonding systems

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Density functional calculations are carried out for the $H_3B–NH_3$ system and compared with experimental and ab initio theoretical data. Calculations that use non-local exchange-correlation potentials are capable of providing excellent geometries, dative bond energies and dipole moments, as well as adequate estimates of vibrational frequencies and barriers to internal rotations. The local density approximation can provide reasonable structure information, but significantly overestimates the dative bond energy, without perturbative non-local corrections.

1. Introduction

The techniques and paradigms of chemical physics have inexorably progressed to larger and more complex chemical and even biochemical systems over the past decade. As experimental investigations continually challenge these complex problems, the need has grown for reliable theoretical techniques that are applicable to large systems. One promising computational tool is density functional theory (DFT) [1,2]. DFT has long been recognized as a valuable tool in the study of extended, metallic systems [1]. Recently, however, expanded applicability in molecular systems has also been noted [3–8]. Systematic investigations of a variety of small, neutral molecules [3–5] have shown that DFT performs reasonably well when compared to ab initio methods. Additional studies have discussed the validity of DFT in calculating dipole moments [6], and hydrogen bonding interactions [7,8]. This paper provides an analysis of another type of chemical bonding to further reference the capabilities and limitations of DFT.

Dative bonds, particularly to electron-deficient main group elements can play an important role in a variety of large molecular systems. For boron in particular there are several classes of molecules [9–13] that take advantage of dative bonds. Boronated

amino acid analogs have a long and rich synthetic history [9,10]. Boronated nucleosides have shown possible pharmaceutical application [11]. Boron-containing heterocycles represent another class of molecules [12,13] with unusual behavior including possible "multipolar" backbones [12]. The systems mentioned here represent just a sample of the possible areas where DFT techniques might find useful applications vis-à-vis dative bonding.

To date, however, DFT has not been characterized as a technique for investigating dative bonding situations involving boron. This paper seeks therefore to determine the behavior of DFT for a small, well-studied system $H_3B–NH_3$, as a reference for the validity of the method. With this reference in hand, applications to larger systems may be more confidently advanced. The $H_3B–NH_3$ molecule has been studied experimentally [14–18] using microwave [14] and X-ray [15] analysis and IR spectroscopy [16,17]. A wide range of ab initio studies has also been carried out [19–30]. Hartree–Fock (HF) level calculations [19–22] have studied the structure, dative bond energy, rotational barrier and vibrational spectrum among other properties. This level of calculation, however, has had mixed success in describing the $H_3B–NH_3$ system, yielding typically high vibrational frequencies [19,23] for example and overestimating the strength of the dative bond [21]. A variety of correlated wavefunctions has also been applied to this system [23–30] yielding improved information for

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the same range of properties as the previously noted HF calculations. Thus, for this system, DFT techniques can be compared with experimental and ab initio (correlated and uncorrelated) investigations for a wide range of properties including equilibrium structure, dative bond strength, barrier to internal rotation, dipole moment and vibrational spectra. By carrying out this comparison we will establish reasonable boundaries on future calculations of larger systems with boron dative bonds, where the more reasonably accurate ab initio calculations are prohibitively expensive.

2. Methodology

All DFT calculations described below were done using the program DMOL [31] with numerical atomic basis functions. These basis functions are represented by an atomic centered, spherical polar mesh [32] with the radial portion of the grid obtained numerically from the solution of the atomic local density functional (LDF) equations. In particular, we use the double numerical basis set augmented by polarization functions, with a "FINE" mesh [31]. This basis is similar to a double-zeta plus polarization basis set in a traditional molecular orbital (MO) calculation. However, because of the use of exact numerical solutions for atoms, this basis set is of significantly higher quality than a normal, polarized double zeta basis set in MO calculations. For instance, it has the correct behavior at the nuclei. As a result, we expect the basis set superposition error should be small.

For local density approximation (LDA) calculations, the form for the exchange correlation energy is of the form of the uniform electron gas assumption, based on the work of von Barth and Hedin [33]. To include non-local exchange-correlation corrections, we employed the Lee–Yang–Parr correlation functional [34] which includes both local and gradient corrected terms and the Becke gradient corrected exchange functional [35]. This combination is denoted as B-LYP. The B-LYP method was in fact found by Johnson, Gill and Pople [3] to give the best overall performance among different DFT functionals in predicting various electronic properties.

Geometries were optimized by using analytical

gradient methods [36]. However, due to the use of numerical methods in both representing the basis functions and calculating various integrals, convergence to a critical point does not necessarily correspond exactly to a point with zero first derivative [37]. This difficulty introduces an error of order 0.001 Å in the calculations of structure. This small error is roughly an order of magnitude smaller than the typical accuracy of DFT methods as compared with experimental structural determinations. Harmonic frequencies were calculated using central differentiation of the analytical gradient with a step size of 0.01 au. Since finite difference derivative calculations (in this case a second derivative) necessarily break the molecular symmetry, degenerate vibrational frequencies are often split by numerical errors. For the H_3B-NH_3 system, we report averaged vibrational frequencies for the degenerate vibrations.

3. Results and discussion

Table 1 provides geometrical data for the H_3B-NH_3 complex using conventional notations for the variables. Comparison with various levels of ab initio calculations as well as the experimentally derived structure are afforded by table 1. DFT provides reasonable structural information at both levels of calculations tested in the present study. Calculations using only the LDA underestimate the length of the dative B–N bond by 4%, but the non-local, B-LYP, calculation provides an excellent geometry in comparison with the gas phase experimental structure, with accuracy comparable to the MP3 optimized structure. The minimal structure is the staggered form. Geometric relaxation for the eclipsed molecule extends the B–N dative bond, a feature seen in every previously reported calculation [20,23]. This evidence suggests therefore, that DFT techniques can provide accurate structural information about dative bonds to boron atoms, particularly when B-LYP level calculations are used. This finding is in line with previous surveys of the accuracy of DFT for other types of chemical bonding systems [3,4].

Vibrational frequency information is provided in table 2. An estimate of the accuracy of this type of information may be important if DFT calculations will ultimately serve as input values for rate calcu-

Table 1
Geometries [a] for H_3B-NH_3

Variable	Hartree–Fock		MP2 6-31G* [d]	MP3 6-31G* [e]	Exp. [f]	DFT	
	STO-3G [b]	6-31G* [c]				LDA [f]	B-LYP [f]
staggered							
r_{BN}	1.657	1.689	1.657	1.664	1.672	1.609	1.675
r_{BH}	1.162	1.209	1.202	1.211	1.210	1.219	1.217
r_{NH}	1.032	1.004	1.014	1.019	1.014	1.033	1.033
α_{HNB}	111.7	110.9	111.0	111.1	109.9	111.5	111.7
α_{HBN}	104.2	104.3	104.4	104.6	104.5	105.3	104.4
eclipsed							
r_{BN}	1.678	1.720		1.690			1.696
r_{BH}	1.161	1.207		1.210			1.211
r_{NH}	1.032	1.003		1.018			1.030
α_{HNB}	111.9	111.1		111.3			111.6
α_{HBN}	104.4	104.4		104.8			104.9

[a] Distances in Å, angles in deg.   [b] Ref. [20].
[c] Ref. [23].   [d] Ref. [24].   [e] Ref. [14].   [f] This work.

Table 2
Vibrational frequencies [a] for H_3B-NH_3

Exp. [b]	HF/4-31G* [c]	HF/6-31G* [d]	DFT/LDA [e]	DFT/B-LYP [e]
232 (6, b_2)	257	198	232.1	268.4
968 (5, a_1)	604	603	745.2	717.3
603 (12, e)	681	681	641.5	642.9
1186 (11, e)	1138	1132	1037.0	1034.1
1052 (4, a_1)	1290	1279	1110.0	1086.3
1301 (10, e)	1303	1293	1180.1	1185.3
1343 (3, a_1)	1446	1484	1318.7	1408.1
1608 (9, e)	1803	1837	1620.0	1664.9
2340 (2, a_1)	2544	2560	2387	2380.9
2415 (8, e)	2589	2604	2456.5	2428.7
3337 (1, a_1)	3692	3691	3327	3292.8
3386 (7, e)	3820	3815	3440.7	3404.5
ZPE=15135	ZPE=16251	ZPE=16270	ZPE=14936	ZPE=14937

[a] Units are cm^{-1}.   [b] Ref. [16] (assignments in parentheses).
[c] Ref. [19].   [d] Ref. [23].   [e] This work.

lations in the larger systems. Notably the values obtained for vibrational frequencies from *both* local and non-local DFT approaches are better than uncorrelated HF calculations in comparison with experimental data, as is most clearly shown via the calculated zero-point energies. It is, however, important to note that the DFT calculated frequencies are harmonic, and anharmonicity is required for precise comparison. The primary conclusion of reasonable accuracy though, should not be affected by the rel-

atively modest corrections anharmonicity would interject at the fundamental level of vibration. Vibrational frequencies for the eclipsed structure are not reported, but confirm that it is a transition state with one imaginary frequency.

The dative bond energy is perhaps the most crucial piece of information that this test must handle adequately. Previous theoretical estimates of this bond strength vary dramatically, with HF level calculations to be on the order of 40 kcal mol^{-1} [21].

Zirz and Ahlrichs [25] determine a value of 27.6 kcal mol^{-1} at the DZP-CEPA2 level of calculation. The MP4(SDTQ)/6-311G**//MP3/6-31G* determination [23] is 34.7 kcal mol^{-1}. Augmenting the basis set for the MP4 level calculation to be 6-311++G(3df, 2p) yields a value of 28.49 kcal mol^{-1} [28]. For the LDA level calculations, this energy is estimated to be 47.0 kcal mol^{-1} which is close to the HF values. Using non-local corrections as perturbative terms, i.e. single-point B-LYP calculations at the LDA calculated geometries, provides dramatic improvement yielding a value of 27.1 kcal mol^{-1}. Optimization at the B-LYP level provides a dative bond energy of 27.6 kcal mol^{-1}. Clearly the value of roughly 27 kcal mol^{-1} determined in the present calculation is very comparable to the above far more expensive correlated ab initio calculations. More importantly, since DFT computational requirements scale as N^3, where N is the number of basis functions, the present results justify the use of DFT techniques for obtaining reliable estimates of dative bond strengths in larger boron containing systems. Furthermore, for very large molecular systems where full optimizations at the B-LYP level of calculation may be prohibitively expensive, the perturbative approach may be used.

For a system such as H_3B-NH_3, perhaps the most formidable calculation to obtain with great accuracy is the barrier to rotation. The experimental [14] estimate for this value is 2.07 kcal mol^{-1}. Binkley and Thornel [23] have done several levels of ab initio calculations to determine this barrier and obtain an estimate of 2.06 kcal mol^{-1} at the best level of calculation. Our B-LYP calculation finds the rotational barrier to be 1.28 kcal mol^{-1}. In contrast to the previously noted tests for structure and energetics, this value is not especially close to correlated wavefunction calculations. It is nonetheless an acceptable, albeit low, estimate for a very difficult calculation.

A final experimentally accessible property that we have calculated is the dipole moment for the system. The measured value for the dipole is 5.22 D [18]. Our calculated value of 5.21 D at the B-LYP level compares very favorably with this value.

4. Summary

We have performed a series of calculations designed to test the validity of the DFT approach to systems containing a dative bond to a boron atom. Our test system of H_3B-NH_3 allows several types of comparisons. DFT calculations using only LDA level calculations are not particularly accurate and should likely be used with some caution. It appears that single-point perturbative corrections for the non-local exchange-correlation potential may provide reasonable energetics for these systems, despite the slight geometrical errors in the LDA calculations. DFT calculations using non-local corrections during optimization, particularly the combination of Becke gradient corrected exchange [35] and Lee–Yang–Parr local and gradient corrected correlation functionals [34], were found to yield very good estimates of several properties including geometry, dipole moment and dative bond energy. Acceptable vibrational frequencies were given by this level of calculation and the barrier to internal rotation was underestimated, but by only 0.7 kcal mol^{-1}. Thus, we conclude that the B-LYP level of calculation can be used with acceptable reliability for the B–N dative bond.

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