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Tests of the MP2 Model and Various DFT Models in Predicting the Structures and B−N Bond Dissociation Energies of Amine−Boranes $(X_3C)_mH_{3-m}B-N(CH_3)_nH_{3-n}$ ($X = H, F$; $m = 0-3$; $n = 0-3$): Poor Performance of the B3LYP Approach for Dative B−N Bonds

Thomas M. Gilbert*

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115

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Computational studies of amine−boranes $(X_3C)_mH_{3-m}B-N(CH_3)_nH_{3-n}$ ($X = H, F$; $m = 0-3$; $n = 0-3$) show that the B3LYP model performs poorly in predicting the structures and B−N bond dissociation energies of such species. A survey of several models shows that the MP2 approach gives the best agreement, but is too computationally intensive for general use. Among several hybrid and pure DFT approaches, the MPW1K model gives the best agreement with experiment and/or with the MP2 model. Scans of the potential surface for rotation around the B−N bond in several molecules and examinations of other amine−boranes suggest that the difficulty with the B3LYP method does not arise from its inability to incorporate nonbonded intramolecular interactions, but from an inherent inability to model the dative bond. The MPW1K approach evidently does this better because it was designed to model “incompletely bound” transition states, which mimic datively bonded systems.

Introduction

Amine−boranes $R_3B-NR'_3$ represent archetypes of compounds containing dative bonds.[1,2] While the dative B−N bond dissociation energies (BDEs) in methylated examples such as $(CH_3)_mH_{3-m}B-N(CH_3)_nH_{3-n}$ were evaluated experimentally many years ago (see Table 2), no similar energetic data have appeared for trifluoromethyl-substituted systems $(CF_3)_mH_{3-m}B-N(CH_3)_nH_{3-n}$. This is unfortunate because Bürger, Pawelke, and co-workers showed that the chemical reactivity of such molecules suggests that they contain far stronger bonds.[3] For example, $(CF_3)_3B-NH(CH_3)_2$ forms through treatment of $[(CF_3)_3B-N(CH_3)_2]^-$ with excess concentrated HCl, and is not further protonated.[4] $(CF_3)_3B-NH(CH_2CH_3)_2$ converts to $(CF_3)_3B-NH_3$ upon treatment with excess $KOH/Br_2/H_2O$.[5] The latter ammine complex is water-soluble and as acidic as NH_4^+ (p$K \approx 5$).[6] It is thus of interest to develop a sense of how strong the bonding is in such donor−acceptor species.

Further motivation arises from our recent computational studies of cycloaddition reactions of aminoboranes $R_2B{=}NR'_2$.[7] While MP2[8] and B3LYP[9] models gave reasonably similar energetic predictions for the parent systems ($R = R' = H$), they differed dramatically for systems where $R = CF_3$ and $R' = CH_3$.[10] Curiously, the B3LYP model predicted higher barriers and less exothermic reactions than did the MP2 model. This contrasted starkly with the usual outcome, wherein the B3LYP model predicts lower barriers than does the MP2 approach.[11]

The data below show that the disparities between predictions by different models are maintained for the series of amine−boranes $(X_3C)_mH_{3-m}B-N(CH_3)_nH_{3-n}$ ($X = F, H$; $m = 0-3$; $n = 0-3$). The B3LYP model predicts less accurate geometries and B−N bond dissociation energies than do other DFT models and the MP2 model. The energetic disparity between the B3LYP and MP2 models increases significantly with the number of F_3C groups on the boron atom. Examination of other DFT models indicates that the related mPW1PW91[12] and MPW1K[11] approaches predict BDEs close to those of the MP2 model, whereas the pure DFT PW91PW91[13] and PBEPBE[14] models perform similarly and slightly worse than do the hybrid models. All DFT models predict BDEs that are lower than the experimental values, while the MP2 model predicts values that tend to be slightly high. The difference presents bounds in which the experimental value likely falls. Scans of the potential surface for rotation around the B−N bond suggest that all models perform similarly in incorporating nonbonded intramolecular forces, so it appears that the inaccurate predictions of the B3LYP model stem from its poor handling of dative bonds. This provides a cautionary tale for workers who routinely use this model without considering its weaknesses. The MPW1K model, which was designed to model transition states, and therefore probably handles “incomplete” bonding more correctly, seems to be the method of choice for predictions involving datively bonded complexes.

Computational Methods

All calculations were performed with the Gaussian 98 suite of programs.[15] Each molecule was fully optimized without constraints using the Hartree−Fock/6-31+G(d) approach. The natures of all stationary point structures were determined by analytical frequency analysis, which also provided zero-point energies (ZPEs). ZPEs were scaled by 0.9153 when used to correct the raw energy values.[16] The structures were then reoptimized using the models given in the Tables and the 6-311++G(d,p) basis set. This basis set was chosen to minimize basis set superposition error (BSSE) while allowing the resource-intensive MP2 calculations to be completed. Counterpoise calculations of representative molecules using hybrid and pure DFT models indicate that the BSSE for the systems studied here varies from about 1.0 to 2.8 kcal mol^{-1}, increasing with increasing BDE. However, since not every case was tested, the BDEs in Table 2 are not corrected for BSSE. One should note that the effect of the correction is to lower the predicted BDE; thus, all DFT models, which generally predict BDEs slightly

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* E-mail: tgilbert@marilyn.chem.niu.edu.

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TABLE 1: Experimental and Predicted [6-311++G(d,p) Basis Set] B−N, B−C, and N−C Bond Distances (Å) for Amine−Boranes $(CH_3)_nH_{3-n}B-N(CH_3)_nH_{3-n}$ and $(CF_3)_nH_{3-n}B-N(CH_3)_nH_{3-n}$ Using Different Models

	expt	MP2	B3LYP	B3PW91	mPW1PW91	MPW1K	PW91PW91	PBEPBE
B−N Distance								
H_3B-NH_3	1.658(2)[a]	1.656	1.666	1.651	1.646	1.638	1.655	1.655
$H_3B-N(CH_3)_3$	1.656(2)[b]	1.641	1.657	1.644	1.639	1.630	1.648	1.648
$(H_3C)_3B-NH(CH_3)_2$	1.656(8)[c]	1.684	1.736	1.713	1.704	1.691	1.717	1.718
$(H_3C)_3B-N(CH_3)_3$	1.70(1)[d]	1.710	1.794	1.757	1.745	1.727	1.765	1.766
$(F_3C)_2HB-N(CH_3)_3$	1.636(8)[e]	1.633	1.653	1.642	1.636	1.625	1.649	1.651
$(F_3C)_3B-NH_3$	1.595(8)[f]	1.605	1.617	1.608	1.604	1.596	1.614	1.615
$(F_3C)_3B-NH_2(CH_3)$	1.589(5)[g]	1.604	1.619	1.611	1.606	1.597	1.617	1.618
$(F_3C)_3B-NH(CH_3)_2$	1.596(8)[g]	1.621	1.640	1.631	1.625	1.614	1.637	1.639
RMS (B−N only)[h]		0.016	0.049	0.033	0.027	0.021	0.037	0.038
AAE (B−N only)[h]		0.014	0.037	0.026	0.022	0.018	0.030	0.031
B−C Distance								
$(H_3C)_3B-NH(CH_3)_2$	1.621(7)	1.625	1.627	1.625	1.623	1.618	1.628	1.630
$(H_3C)_3B-N(CH_3)_3$	1.69(4)	1.627	1.626	1.625	1.623	1.619	1.628	1.630
$(F_3C)_2HB-N(CH_3)_3$	1.597(7)	1.629	1.636	1.633	1.630	1.624	1.635	1.637
$(F_3C)_3B-NH_3$	1.612(9)	1.621	1.633	1.631	1.627	1.620	1.634	1.636
$(F_3C)_3B-NH_2(CH_3)$	1.615(6)	1.626	1.637	1.635	1.632	1.624	1.638	1.640
$(F_3C)_3B-NH(CH_3)_2$	1.613(6)	1.631	1.645	1.642	1.642	1.631	1.645	1.647
N−C Distance								
$H_3B-N(CH_3)_3$	1.485(1)	1.481	1.487	1.479	1.476	1.466	1.489	1.490
$(H_3C)_3B-NH(CH_3)_2$	1.466(9)	1.481	1.484	1.477	1.473	1.464	1.486	1.487
$(H_3C)_3B-N(CH_3)_3$	1.47(1)	1.483	1.487	1.479	1.476	1.467	1.489	1.489
$(F_3C)_2HB-N(CH_3)_3$	1.476(6)	1.495	1.502	1.493	1.489	1.479	1.503	1.503
$(F_3C)_3B-NH_2(CH_3)$	1.507(5)	1.495	1.501	1.491	1.488	1.479	1.500	1.500
$(F_3C)_3B-NH(CH_3)_2$	1.509(8)	1.499	1.506	1.496	1.492	1.483	1.505	1.505
RMS (all)[h]		0.021	0.037	0.029	0.026	0.024	0.032	0.032
AAE (all)[h]		0.016	0.028	0.023	0.021	0.018	0.025	0.026

[a] Thorne, L. R.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1983**, *78*, 167−171. Microwave study. [b] Iijima, K; Adachi, N.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3269−3273. Gas-phase electron diffraction study. [c] Ouzounis, K.; Riffel, H.; Hess, H. *J. Organometallic Chem.* **1987**, *332*, 253−258. Single-crystal X-ray diffraction study. [d] Kuznesof, P. M.; Kuczkowski, R. L. *Inorg. Chem.* **1978**, *17*, 2308−2311. Microwave study. [e] Brauer, D. J.; Pawelke, G. *J. Organometallic Chem.* **1995**, *486*, 129−134. Single-crystal X-ray diffraction study of $(F_3C)_2HB-N(CH_3)_2(CH_2Ph)$. [f] Ansorge, A.; Brauer, D. J.; Burger, H.; Krumm, B.; Pawelke, G. *J. Organometallic Chem.* **1993**, *446*, 25−35. Single-crystal X-ray diffraction study. [g] Ref 4. Single-crystal X-ray diffraction studies of $(F_3C)_3B-NH_2(CH_2CH_3)$ and $(F_3C)_3B-NH(CH_2CH_3)_2$. [h] $RMS = [\Sigma(x - x_{expt})]^2/N]^{1/2}$; $AAE = |x - x_{expt}|/N$.

lower than the experimental values, actually perform slightly worse than the level reflected in the rms deviations and average absolute errors given in Table 2.

Results and Discussion

Structures of the $(F_3C)_nH_{3-n}B-NR_3$ Molecules. Several examples of methyl- and trifluoromethyl-substituted amine−borane complexes have been structurally characterized. A comparison of the B−N, B−C, and N−C bond distances determined by experiment and predicted by several model chemistries appears in Table 1.

One sees that the MP2 model predicts both the bond distances most accurately of the models tested, performing particularly well in predicting the dative B−N bond length. In contrast, the B3LYP model performs worst, predicting exceptionally long B−N bond lengths in several cases.[17] The other DFT approaches fall between the two, with the hybrid mPW1PW91 and MPW1K models achieving results similar to those of the MP2 model at substantially less resource cost. The latter hybrid, designed to model the energetics of transition states and thus probably exceptionally capable of modeling datively bound systems such as these, performs particularly well.

That the B3LYP model struggles in predicting the dative B−N distance more than the other covalent bond distances is evident from a comparison of the RMS and AAE values for the B−N bond only with those for the combined bond distances. It can be seen in Table 1 that the MP2 model predicts the B−N bond distances better than it does the bond distances overall; the RMS error increases 0.005 Å from the smaller set to the larger set. By contrast, the B3LYP RMS error drops by 0.012 Å when all the bond distances are used in the calculation, by far the largest change of any model. This implies that the B3LYP model will accurately predict the structures of organic molecules or molecules containing many “organic” covalent bonds (such as main-group or transition-metal organometallics), but may perform far more poorly for systems where bonding is dative in nature.

One notes that all the models generally predict longer B−N bonds for amine−boranes than those observed in the single crystal studies. This particularly applies to $(CH_3)_3B-NH(CH_3)_2$, but holds for all the solid-state cases. The phenomenon probably arises from crystal packing forces compressing the B−N bond, reflecting the flat potential associated with this motion. The amine−borane H_3B-NH_3 allows an experimental comparison, as the solid-state neutron diffraction study gave $d(B-N) = 1.58(2)$ Å,[18] while a microwave study gave $d(B-N) = 1.658(2)$ Å. The difference of 0.07 Å between the studies is larger than the difference between the experimental and computationally predicted values for any amine−borane studied here.

Amine−Borane B−N Bond Dissociation Energies. A comparison of experimental and theoretical BDEs appears in Table 2. The experimental data are limited, but provide a picture of the effect of substitution on the boron and nitrogen atoms on the BDEs. One sees that the values are in keeping with qualitative expectations. Adding methyl groups to the nitrogen increases its Lewis basicity and thereby the BDEs, although the trimethylamine adducts show a decrease in BDE.[2] Adding methyl groups to the boron, decreasing its Lewis acidity, decreases the BDEs. The latter effect is far larger than the former.

TABLE 2: Experimental and Predicted [6-311++G(d,p) Basis Set] B−N Bond Dissociation Energies (kcal mol^{-1}) for Amine−Boranes $(CH_3)_nH_{3-n}B-N(CH_3)_nH_{3-n}$ and $(CF_3)_nH_{3-n}B-N(CH_3)_nH_{3-n}$ Using Different Models

	expt	MP2	B3LYP	B3PW91	mPW1PW91	MPW1K	PW91PW91	PBEPBE
H_3B-NH_3	31.1(1.0)[a]	26.5	23.5	26.5	27.8	28.1	29.5	29.4
$H_3B-NH_2(CH_3)$	35.0(0.8)[a]	32.3	27.8	30.7	32.2	32.6	34.1	33.9
$H_3B-NH(CH_3)_2$	36.4(1.0)[a]	35.6	29.0	31.9	33.6	34.2	35.4	35.2
$H_3B-N(CH_3)_3$	34.8(0.5)[a]	36.8	27.8	30.9	32.8	33.6	34.3	34.0
$(CH_3)_3B-NH_3$	13.8(0.3)[b]	15.4	6.4	8.8	10.7	11.7	11.6	11.2
$(CH_3)_3B-NH_2(CH_3)$	17.6(0.2)[b]	20.4	8.7	10.9	13.2	14.4	14.3	13.9
$(CH_3)_3B-NH(CH_3)_2$	19.3(0.2)[b]	22.1	7.0	9.3	11.9	13.4	13.1	12.5
$(CH_3)_3B-N(CH_3)_3$	17.6(0.2)[b]	21.4	2.3	4.9	7.7	9.6	8.8	8.1
RMS_{expt}[c]		2.9	9.6	7.1	5.1	4.1	4.1	4.5
AAE_{expt}[c]		2.6	9.1	6.5	4.4	3.5	3.1	3.4
$(F_3C)H_2B-NH_3$		40.4	35.1	37.8	39.6	40.5	40.5	40.1
$(F_3C)H_2B-NH_2(CH_3)$		46.5	39.6	42.1	44.1	45.2	45.1	44.7
$(F_3C)H_2B-NH(CH_3)_2$		49.3	39.9	42.3	44.5	45.8	45.6	45.1
$(F_3C)H_2B-N(CH_3)_3$		48.6	36.7	39.0	41.5	43.1	42.5	41.8
$(F_3C)_2HB-NH_3$		52.6	44.5	46.9	49.1	50.9	48.9	48.3
$(F_3C)_2HB-NH_2(CH_3)$		58.8	48.6	50.6	53.2	55.0	53.3	52.5
$(F_3C)_2HB-NH(CH_3)_2$		60.5	47.6	49.3	52.2	54.3	52.5	51.6
$(F_3C)_2HB-N(CH_3)_3$		58.6	41.9	43.6	47.0	49.6	47.1	46.0
$(F_3C)_3B-NH_3$		62.6	51.6	53.6	56.3	58.8	55.2	54.4
$(F_3C)_3B-NH_2(CH_3)$		69.1	54.7	56.3	59.5	62.3	58.7	57.8
$(F_3C)_3B-NH(CH_3)_2$		69.5	51.7	52.8	56.6	59.6	56.0	54.8
$(F_3C)_3B-N(CH_3)_3$		67.7	45.3	46.5	50.8	54.5	50.1	48.6
RMS_{MP2}[c]			12.3	10.5	8.1	6.3	7.9	8.6
$RMS(CF_3)_{MP2}$[c]			13.1	11.5	8.7	6.5	8.9	9.7
$(NC)_3B-N(CH_3)_3$		60.9	41.4	45.4	48.8	53.1	45.5	45.0
$(Cl_3C)_2BH-N(CH_3)_3$		36.5	14.2	16.8	19.3	23.8	16.8	15.8

[a] Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992−1007. [b] Brown, H. C.; Bartholomay, H., Jr.; Taylor, M. D. *J. Am. Chem. Soc.* **1944**, *66*, 435−442. [c] $RMS_{expt} = [\Sigma(x - x_{expt})]^2/N]^{1/2}$; $AAE_{expt} = |x - x_{expt}|/N$; $RMS_{MP2} = [\Sigma(x - x_{MP2})]^2/N]^{1/2}$; $RMS(CF_3)_{MP2} = [\Sigma(x - x(CF_3)_{MP2})]^2/N]^{1/2}$, where only the 12 complexes containing a CF_3 substituent are used.

The MP2 model predicts the BDEs well. Since the predictions are sometimes too high, including the lowering effect of basis set superposition error would improve the agreement, especially for the trimethylborane series. In contrast, the B3LYP model consistently predicts BDEs lower than found experimentally, sometimes remarkably so. The theoretical B3LYP BDE for $(H_3C)_3B-N(CH_3)_3$ (2.3 kcal mol^{-1}), for example, is so low that if it were correct, the amine−borane would probably exhibit poor room-temperature stability. This is, of course, untrue.

The other DFT models also predict BDEs that are too small, but all are closer to correct than the B3LYP values. One sees in particular that the models are 9−10 kcal mol^{-1} off for $(H_3C)_3B-N(CH_3)_3$. The most accurate hybrid DFT model is the MPW1K approach, again probably because it was created to model incompletely bound systems. In this regard, the mPW1PW91 model, which differs from the MPW1K model only in the degree of exact exchange, predicts BDEs less accurately by ca. 1 kcal mol^{-1}. The pure DFT PW91PW91 and PBEPBE models perform essentially identically to the MPW1K model in predicting the BDEs for these parent and methyl-substituted amine−boranes.

However, the pure DFT models perform less well when applied to trifluoromethyl-substituted amine−boranes. One sees in Table 2 the unsurprising prediction that, as the number of F_3C substituents on the boron atom increases (thereby increasing its Lewis acidity), the BDE increases. The increases are generally linear, with slopes ranging from 10 to 12 kcal mol^{-1} for the MP2 model to 4−9 kcal mol^{-1} for the DFT cases. The $(F_3C)_3B-NH_n(CH_3)_{3-n}$ complexes exhibit BDEs of ca. 55−70 kcal mol^{-1} depending on the model, large enough to be consistent with their experimental stabilities. It can be further seen that the energy difference between BDEs predicted by the MP2 and the DFT methods increases as the number of F_3C substituents on the boron atom increases. The B3LYP model shows the most extreme behavior, with a gap that expands by 3−4.5 kcal mol^{-1} per F_3C group. This results in particularly poor agreement between the B3LYP and MP2 models for $(F_3C)_3B-N(CH_3)_3$, where the two BDE predictions differ by 22 kcal mol^{-1}. The other DFT models also suffer from this problem, although not as greatly. The MPW1K model least exhibits this tendency (the gap is ca. 0.7−3 kcal mol^{-1}), and so gives a BDE prediction for $(F_3C)_3B-N(CH_3)_3$ that differs from the MP2 value by only 13 kcal mol^{-1}. Overall, the RMS difference between the BDE predictions of the MP2 model and the DFT models is greatest for the B3LYP model (12−13 kcal mol^{-1}) and smallest for the MPW1K model (6.3−6.5 kcal mol^{-1}), with the other DFT models at least 1 kcal mol^{-1} less in agreement than the MPW1K approach (Table 2). To the extent that the MP2 model predicts the BDEs most accurately, it seems that the MPW1K method provides the best combination of accuracy and resource-efficient computations.

Why the B3LYP model performs so poorly for datively bonded molecules while performing so well for many other systems in not immediately evident. Indeed, recent work from Handy et al. suggests that this approach combined with a triple-ζ basis set is among the best models for predicting the structures and energetics of a modified G2 test set.[19] However, Tsuzuki and Lüthi showed that the B3LYP approach does not handle weak intermolecular interactions well, and suggested the B3PW91 model as an alternative.[20] One could envision that the B3LYP model fails for trifluoromethyl-substituted amine−boranes because it does not incorporate intramolecular through-space fluorine−hydrogen interactions well.

This possibility was tested by using different models to scan the potential surface for rotation about the B−N bond of $(F_3C)H_2B-NH_2(CH_3)$, $(F_3C)H_2B-NH(CH_3)_2$, $(F_3C)_2HB-NH_2(CH_3)$, and $(F_3C)_2HB-NH(CH_3)_2$.[21] As representative of the set, the scan data for $(F_3C)_2HB-NH(CH_3)_2$ appear graphically in Figure

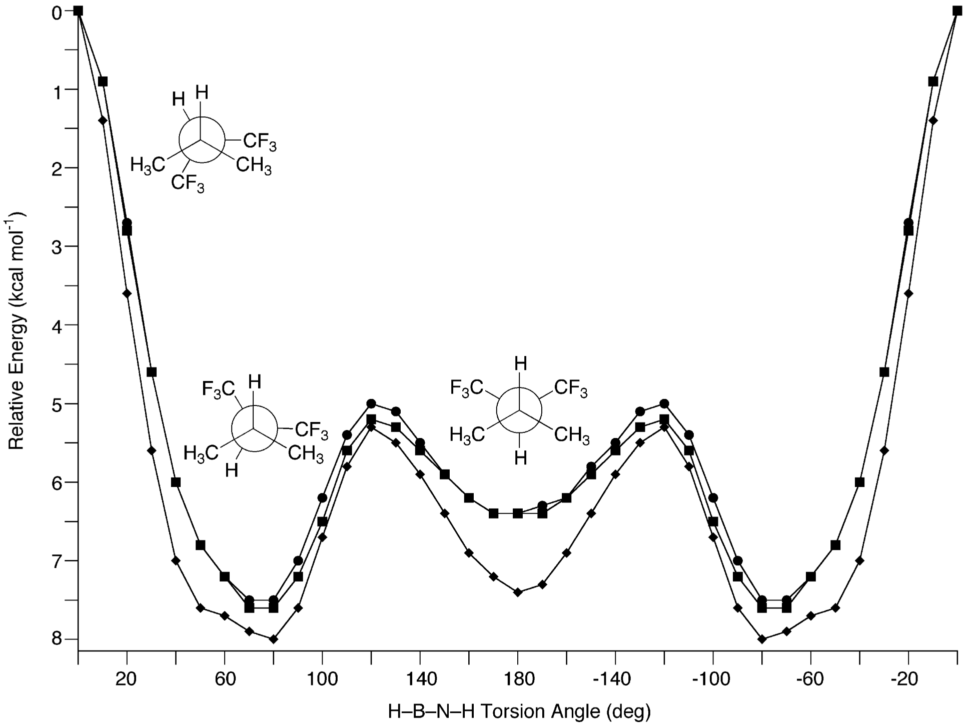

Figure 1. Relative energies [6-31+G(d) basis set] for rotation about the B−N bond in $(F_3C)_2HB-NHMe_2$. Structures are given to indicate the orientation of the substituents at different points along the rotation path. The symbol ■ indicates the B3LYP hybrid DFT model, ● indicates the pure DFT mPWPW91 model, and ◆ indicates the MP2 model.

1. One sees that the models differ slightly in the extent to which rotation affects the molecular energy. However, the difference is far smaller than that between the BDEs determined using, for example, the MP2 and B3LYP models. Furthermore, all three models predict a global minimum containing a slightly gauche orientation of the substituents (H−B−N−H = 70−80°), indicating that the three "see" the nonbonded interactions similarly. It thus appears that the ability of the models to incorporate intramolecular nonbonded interactions does not account for the energetic disparities.

This view is substantiated by the BDEs calculated for $(NC)_3B-N(CH_3)_3$ and $(Cl_3C)_2HB-N(CH_3)_3$. The former was selected as a candidate for study because the cyano functional group appears to withdraw electrons about as well as the F_3C group does,[22] but its linear structure means that it cannot readily "point" a component atom toward an $N(CH_3)_3$-moiety hydrogen atom. The latter was selected because the longer C−Cl distances present could allow for increased intramolecular nonbonded interactions with the methyl hydrogen atoms.

As can be seen in Table 2, both compounds show sizable disparities between the BDEs predicted by the MP2 and B3LYP models, with the other models suggesting values between these, and the MPW1K model giving the value closest to that of the MP2 approach. Since the BDEs for $(NC)_3B-N(CH_3)_3$ are about the same as the BDEs for $(F_3C)_3B-N(CH_3)_3$, it appears that the possible intramolecular interactions between F and H atoms in the latter contribute little to the BDE. Instead, it seems the BDEs are more determined by the Lewis acidities of the borane moieties, which are evidently similar. By extension this implies that the cyano group in the tricyanoborane complex indeed withdraws electron density from the boron atom as effectively as does the F_3C group in the tris(trifluoromethyl)borane complex. The Cl_3C group clearly does not behave as a good electron-withdrawing group, since the BDEs for $(Cl_3C)_3B-N(CH_3)_3$ are approximately half those of $(F_3C)_3B-N(CH_3)_3$. If the Cl and methyl H atoms interact intramolecularly, the energetic impact of the interaction seems minimal at most.

It therefore seems that the poor performance of the B3LYP model stems nearly entirely from its inability to adequately describe dative bonds. This apparently has not previously been noted. As mentioned, workers have observed problems with B3LYP predictions of the strength of hydrogen bonds and van der Waals interactions,[20] but bonding of the type examined here has not been surveyed. It is certain from these results that future studies involving dative bonds should employ multiple models to ensure that energetic bounds are determined. The MPW1K model appears to be an excellent choice in combining accuracy with computation speed.

Conclusions

The work here indicates that the B3LYP model performs poorly when applied to the study of dative B−N bonds. This stands in contrast to the work of Handy et al., who found the B3LYP/triple-ζ model to perform best of the common DFT approaches for an expanded G2 test set.[19] One notes that the test set does not contain amine−boranes, or indeed any systems that contain clearly dative bonds (by the Haaland definition).[2] As a result, it is recommended that workers studying molecules containing dative bonds employ several model chemistries to check their results. If usable, the MP2 approach gives good agreement with experiment. If the computational demands are too large for MP2, the MPW1K approach, since it was designed for "incompletely bound" transition states, appears excellent for such work. Finally, it should be noted that "dative" does not mean "weak" in the context of the bonding studied here, and the B3LYP model cannot be forgiven for its performance because the bonding is weak. It seems to predict strong dative bond energies more incorrectly than it predicts weak dative bond energies.

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(17) A reviewer expressed concern about the data used to make this comparison, noting that the B−N and B−C distances predicted by the B3LYP model for $H_3B{-}N(CH_3)_3$ agree well with those determined in the gas-phase electron diffraction study, and that several of the experimental structures employed arise from solid-state studies. It was implied that solid-state distances might not be good baselines for testing the merits of “gas-phase” theoretical models. By way of rebuttal, one should note that *all* the theoretical models are “gas phase”, so that if theoretical/experimental comparisons are invalid, they should be invalid for all models; i.e., no model should predict the bond distances well. Here, the MP2, mPW1PW91, and MPW1K models adequately predict the bond distances. Moreover, if one limits the comparison to only the three molecules for which gas-phase structures were determined experimentally [$H_3B{-}NH_3$, $H_3B{-}N(CH_3)_3$, and $(CH_3)_3B{-}N(CH_3)_3$], the MP2 model still performs best, with an RMS deviation for the B−N distances (RMS_{BN}) of 0.010 Å and an RMS deviation for all non-hydrogen bond distances (RMS_{all}) of 0.025 Å. The B3LYP model performs worst, with $RMS_{BN} = 0.054$ Å, $RMS_{all} = 0.044$ Å. The large difference derives mostly from the exceptionally poor agreement between the B3LYP model and experiment in evaluating the B−N bond in $(CH_3)_3B{-}N(CH_3)_3$ (see Table 1). The MPW1K model gives the second most accurate prediction of the B−N distances ($RMS_{BN} = 0.025$ Å), while the other DFT models give $RMS_{BN} = 0.029{-}0.038$ Å. However, all the DFT models save B3LYP perform nearly identically for the entire collection of non-hydrogen bond distances: $RMS_{all} = 0.032{-}0.035$ Å.

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