

Comparative calculations of complexation enthalpies between Lewis bases and borontrifluoride

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Abstract. Complexation enthalpies were calculated for complexes of eight Lewis bases – dimethyl ether, diethyl ether, ethyl acetate, trimethylamine, trimethylphosphine, tetrahydropyran, tetrahydrofuran, and tetrahydrothiophene with BF_3 using HF/6-311+G**, B3LYP/6-311+G**, MP2/6-311+G**, MP2/6-311+G(2df,2pd), G2(MP2), and CBS-QB3 methods and compared to experimentally determined ones. The best results were obtained with the CBS-QB3 method. Application of the BSSE correction by the counterpoise method overcorrected the error and gave systematically too low enthalpy values. B3LYP/6-311+G** calculations seem to be best suited for investigating trends in BF_3 affinities of different bases in the sense of compromise between speed and accuracy, while CBS-QB3 can be recommended for the calculation of absolute complexation energies between BF_3 and Lewis bases.

Key words: Lewis basicity, BF_3 , DFT calculations, ab initio calculations.

INTRODUCTION

Donor–acceptor complexes between Lewis acids and bases play a very important role in many catalytic reactions. For example, nucleophilic substitution, elimination, and addition reactions are often catalysed by an initial electrophilic attack on the substrate. The role of the electrophile is here to form an intermediate complex with the substrate, thereby increasing its reactivity toward the desired nucleophile. One often used electrophilic catalyst is borontrifluoride (BF_3). The efficiency of catalysis depends on the acid/base properties of both electrophile and substrate. Scales of Lewis basicity have been established from experimental complexation enthalpies toward BF_3 and a number of other Lewis acids.

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Another alternative for predicting the complexation energies between BF_3 and different bases is by quantum chemical or density functional theory calculations, which can provide a wide range of information (energetical, structural, etc.) for the studied systems. Indeed, many theoretical studies have been devoted to the complexes between BF_3 and various bases.

Rauk et al. [1] studied interactions between BF_3 and 17 oxygen bases employing geometry optimizations at the HF/6-31G* level followed with single point energy calculations at the MP3/6-31G* and MP2/6-31G* levels. Jonas et al. [2] compared donor-acceptor complexes of the Lewis acids BH_3 , BF_3 , BCl_3 , AlCl_3 , and SO_2 with calculations at the MP2/TZ2P level. Jiao & Schleyer [3] used SCRF calculations at the HF/6-31+G* level to investigate the effect of the medium on the HCN-BF_3 bond length. Morales [4] studied the interactions between BF_3 and dimethyl and perfluorodimethyl ether with AM1 calculations. Weak complexes between ethene, propene, ethyne, and propyne and BF_3 were studied by van der Veken's group by IR spectroscopy and MP2/6-31+G* calculations [5, 6]. Rayón & Sordo [7] studied the nature of the interaction in donor-acceptor van der Waals complexes of borontrifluoride with carbon monoxide and ammonia at the MP2/6-31G** level. Cho & Cheong [8] studied the structure and vibrational frequencies of the $\text{CH}_3\text{CN-BF}_3$ complex by MP2/6-31+G(2d,p) calculations. Coxon & Thorpe [9] studied the mechanism of the BF_3 catalysed rearrangement of 2,2,3-trimethyl-1,2-epoxybutane to 2,3,3-trimethylbutanal by B3LYP/6-31G* calculations. Pyridine- BF_3 complex was studied by Meng and coworkers [10] with B3LYP/6-311+G* calculations. Khavasi et al. [11] studied complexes between porphine and BF_3 using HF, B3LYP, and MP2 calculations with basis sets up to 6-31G*. B3PW91 and MP2 calculations with aug-cc-pvdz and aug-cc-pvtz basis sets were employed by Dobrowolski & Kawecki [12] to study the structure of the sulfinimine MeS(O)=CHMe with BF_3 .

The examples given in the previous paragraph illustrate the wide variation in systems calculated in connection with BF_3 complexes and also the variety of computational methods used for this purpose. However, to the best of our knowledge, no systematic study of the applicability of different methods for such studies have appeared to guide the investigator in picking the right method. Undoubtedly, one of the reasons for this is very scarce experimental data about the gas-phase complexation energies for such complexes. In contrast, much more solution-phase data are available [13]. However, to choose a right methodology for liquid-phase calculations, first a good calibration for the gas phase is needed.

We have carried out a comparative study of the gas-phase complexation enthalpies obtained by the HF/6-311+G**, B3LYP/6-311+G**, MP2/6-311+G**, MP2/6-311+G(2df,2pd), G2(MP2), and CBS-QB3 methods. Experimental gas-phase complexation enthalpies were found in the literature for dimethyl ether [14], diethyl ether [14], ethyl acetate [15], trimethylamine [16], trimethylphosphine [17], tetrahydropyran [18], tetrahydrofuran [18], and tetrahydrothiophene [19]. So the complexes of BF_3 with those bases (see Fig. 1) were studied.

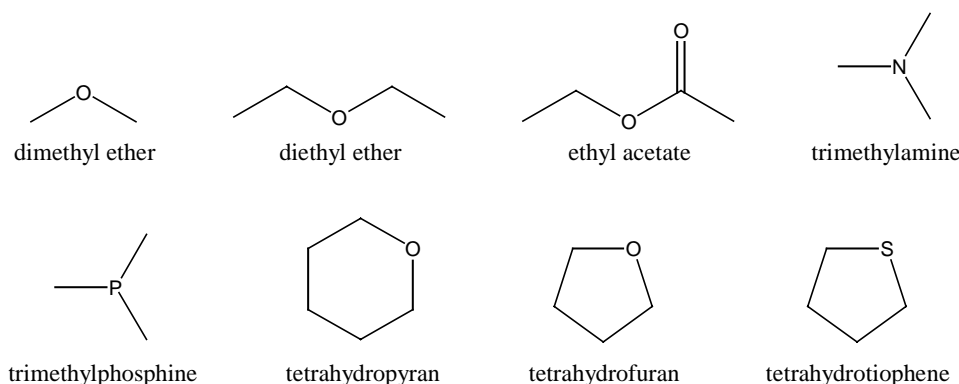


Fig. 1. Structure of the studied bases.

METHODS

All calculations were carried out with the Gaussian 03 program package [20]. Geometries were fully optimized and the frequencies calculated at respective levels. All stationary points were found to be true minima (number of imaginary frequencies, NImag = 0). The calculated frequencies were used for calculations of the enthalpies.

The enthalpy of complex minus the enthalpies of the base and BF_3 is the directly calculated complexation enthalpy, $\Delta H_{\text{complexation}}$.

$$\Delta H_{\text{complexation}} = H(\text{B} \cdot \text{BF}_3)_{ab}^* - H(\text{BF}_3)_a - H(\text{B})_b, \quad (1)$$

where $H(\text{B} \cdot \text{BF}_3)$, $H(\text{BF}_3)$, and $H(\text{B})$ are enthalpies of $\text{B} \cdot \text{BF}_3$, BF_3 , and B , respectively, calculated at their optimized geometries. The calculated complexation enthalpies are given in Table 1.

It is well known that calculations of complexation energies are always shadowed by the basis set superposition error (BSSE, artificial lowering of the total energy of the complex that arises from the mathematical fact that the basis sets are not complete and thus the basis functions of one component of the complex are available for the description of the electron density of the second one [21]). The magnitude of the BSSE can be estimated by the counterpoise (CP) correction by Boys & Bernardi [22]. The CP correction is defined as

$$\Delta E_{\text{CP}} = E(\text{A})_{ab} + E(\text{BF}_3)_{ab} - E(\text{A})_a - E(\text{BF}_3)_b, \quad (2)$$

where $E(\text{A})_{ab}$ and $E(\text{BF}_3)_{ab}$ are the monomer energies with the basis set of the complex, $E(\text{A})_a$ and $E(\text{BF}_3)_b$ are the monomer energies with their normal basis sets. Here the monomers are calculated with the geometry they have in the complex in all cases. The counterpoise corrected complexation enthalpy, ΔH_{BSSE} , is given as

Table 1. Calculated complexation energies (ΔH , in kJ/mol) of the studied Lewis bases with BF_3 . ΔH_{BSSE} is complexation energy corrected for BSSE

Compound	HF/6-311+G**		B3LYP/6-311+G**		MP2/6-311+G**		MP2/6-311G (2df,2pd)		G2(MP2)		CBS-QB3		Exp
	ΔH_{calc}	ΔH_{BSSE}	ΔH_{calc}	ΔH_{BSSE}	ΔH_{calc}	ΔH_{BSSE}	ΔH_{calc}	ΔH_{BSSE}	ΔH_{calc}	ΔH_{BSSE}	ΔH_{calc}	ΔH_{BSSE}	
Trimethylamine	-90.4	-78.1	-98.3	-89.2	-134.9	-93.9	-131.7	-104.0	-131.6	-131.3	-111.3	[16]	
Trimethylphosphine	-36.1	-28.1	-53.1	-46.4	-68.2	-35.9	-61.8	-42.2	-64.4	-65.6	-79.1	[17]	
Tetrahydrofuran	-53.3	-40.9	-56.0	-46.2	-80.1	-41.8	-75.6	-51.6	-76.4	-74.5	-70.3	[18]	
Tetrahydropyran	-48.8	-36.3	-53.0	-43.1	-76.9	-37.8	-73.6	-48.9	-73.7	-71.6	-64.5	[18]	
Dimethyl ether	-16.9	-5.8	-44.2	-34.8	-67.5	-31.9	-63.8	-42.2	-64.3	-61.7	-57.1	[14]	
Ethyl acetate	-37.0	-25.9	-41.0	-33.6	-52.7	-20.0	-55.8	-34.5	-55.8	-55.7	-53.6	[15]	
Diethyl ether	-32.0	-19.2	-37.2	-27.3	-64.3	-23.9	-60.5	-35.1	-61.7	-61.9	-49.9	[14]	
Tetrahydrothiophene	-12.2	-3.4	-28.8	-22.2	-48.1	-15.3	-43.9	-24.0	-45.0	-41.6	-21.8	[19]	

$$\Delta H_{\text{BSSE}} = \Delta H_{\text{complexation}} - \Delta E_{\text{CP}}. \quad (3)$$

Application of CP correction always lowers the complexation energy. For the G2(MP2) and CBS-QB3 methods the correction should be negligible as those methods are effectively extrapolating to the infinite (complete) basis set. Table 1 gives also BSSE corrected complexation enthalpies.

RESULTS AND DISCUSSION

Average absolute errors, squares of correlation coefficients, and correlation equations are given in Table 2 and the correlations are graphically represented in Fig. 2.

Usually HF and B3LYP complexation enthalpies are smaller in absolute values than experimental ones, while those calculated at the MP2, G2(MP2), and CBS-QB3 levels are (except for trimethylphosphine) larger than the reported experimental ones. Average absolute errors in calculated complexation energies decrease in the order HF/6-311+G** > B3LYP/6-311+G** \approx MP2/6-311+G** > MP2/6-311+G(2df,2pd) \approx G2(MP2) > CBS-QB3 from 22.6 kJ/mol to 10.4 kJ/mol. It is notable that the three last methods gave very close complexation energies (within 4 kJ/mol to CBS-QB3) and even MP2/6-311+G** results are surprisingly close to those of CBS-QB3 (within 6.6 kJ/mol), indicating convergence of the complexation energies.

Inspection of squares of correlation coefficients (R^2) in Table 2 indicates that the correlations between experimental and calculated complexation energies are modest (always below 0.9). Somewhat surprisingly the best correlation is obtained at the B3LYP/6-311G** level, but it seems to be a result of fortuitous cancellation of errors. The slopes of correlation lines are all less than one and intercepts are not zeroes (slope one and zero intercept correspond to ideal correlation, free of systematic errors). It should be noted, however, that in most

Table 2. Average absolute errors, squares of correlation coefficients, and equations for correlations between experimental (ΔH_{exp}) and calculated (ΔH_{calc}) complexation energies between Lewis bases and BF_3 . All values are in kJ/mol

	Average absolute errors	Squares of correlation coefficient R^2	Correlation equation
HF/6-311+G**	22.6	0.7809	$\Delta H_{\text{calc}} = (0.840 \pm 0.182) * \Delta H_{\text{exp}} + (12.440 \pm 12.323)$
B3LYP/6-311+G**	13.8	0.8944	$\Delta H_{\text{calc}} = (0.772 \pm 0.108) * \Delta H_{\text{exp}} + (-2.435 \pm 7.351)$
MP2/6-311+G**	13.6	0.8000	$\Delta H_{\text{calc}} = (0.933 \pm 0.190) * \Delta H_{\text{exp}} + (-14.892 \pm 12.921)$
MP2/6-311+G(2df,2pd)	11.7	0.7946	$\Delta H_{\text{calc}} = (0.918 \pm 0.191) * \Delta H_{\text{exp}} + (-12.585 \pm 12.931)$
G2(MP2)	11.8	0.8084	$\Delta H_{\text{calc}} = (0.913 \pm 0.182) * \Delta H_{\text{exp}} + (-13.649 \pm 12.320)$
CBS-QB3	10.4	0.8383	$\Delta H_{\text{calc}} = (0.946 \pm 0.170) * \Delta H_{\text{exp}} + (-10.488 \pm 11.504)$

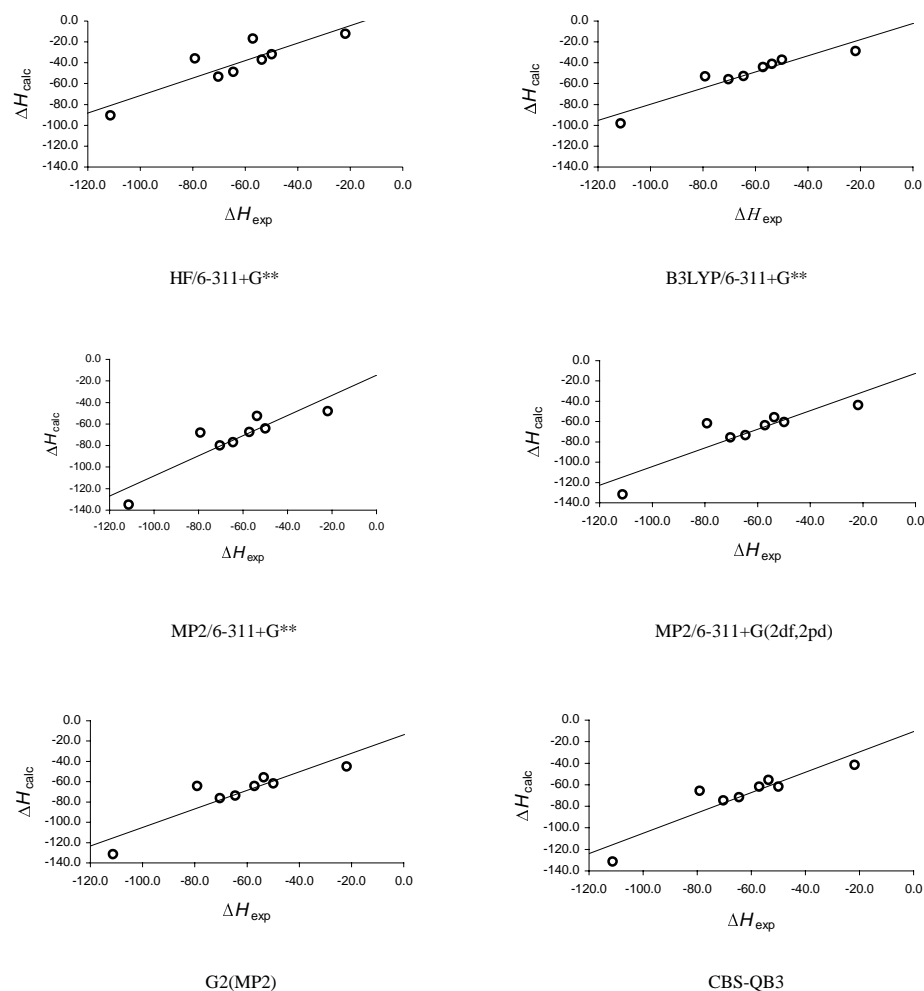


Fig. 2. Correlations between calculated (ΔH_{calc}) and experimental (ΔH_{exp}) complexation energies between Lewis bases and BF_3 . All values are in kJ/mol.

cases the slopes deviate from unity less than their standard error. The only exception is the B3LYP/6-311G** method, with the slope 0.772 ± 0.108 , indicating a serious systematic error. A similar situation occurs also for the intercepts that are in the range from -2 to -18 kJ/mol, with the standard errors in the range of these values. The closest match with ideal parameters (zero intercept and unity slope) was obtained for the most sophisticated CBS-QB3 method ($\Delta H_{\text{C}} = (0.946 \pm 0.170) * \Delta H_{\text{E}} - (10.488 \pm 11.504)$).

Calculations of complexation energies are always shadowed by the basis set superposition error as described above. We applied the BSSE correction to our HF, B3LYP, and MP2 results. The resulting complexation energies are now

usually smaller than experimental ones and the absolute average error has grown (compared to uncorrected value), indicating that the CP correction clearly overcorrects the BSSE in a nonsystematic manner. As seen from Table 3, the R^2 values are somewhat improved by that procedure (except for B3LYP). At the same time the slopes have somewhat diminished (farther from ideal values). The intercepts have grown considerably (and changed the signs, being now in the range from +6 to +22 kJ/mol). Based on these data application of BSSE correction seems to be unjustified.

As seen from Fig. 2, the point corresponding to trimethylphosphine always deviates from the correlation line by several tens of kJ/mol. We repeated our correlation analysis omitting this one point. The results of such analysis are presented in Tables 4 and 5. As a result we got much better correlations (R^2 values are now 0.87–0.94 without and 0.86–0.92 with BSSE correction), slopes are close (within standard error) to unity, and intercepts are smaller (in absolute values). The BSSE corrections do not improve here the R^2 values, they diminish the slope and increase the intercept (farther from ideal values). Again, it seems that the application of BSSE correction does not improve the correlation.

Table 3. Average absolute errors, squares of correlation coefficients, and equations for correlations between experimental (ΔH_{exp}) and calculated (ΔH_{calc}) complexation energies (including BSSE) between Lewis bases and BF_3 . All values are in kJ/mol

	Average absolute errors	Squares of correlation coefficient R^2	Correlation equation
HF/6-311+G**	33.7	0.7985	$\Delta H_{\text{calc}} = (0.820 \pm 0.168)^* \Delta H_{\text{exp}} + (22.285 \pm 11.406)$
B3LYP/6-311+G**	20.7	0.8876	$\Delta H_{\text{calc}} = (0.756 \pm 0.110)^* \Delta H_{\text{exp}} + (5.113 \pm 7.451)$
MP2/6-311+G**	25.9	0.8264	$\Delta H_{\text{calc}} = (0.867 \pm 0.162)^* \Delta H_{\text{exp}} + (17.441 \pm 11.006)$
MP2/6-311+G(2df,2pd)	16.2	0.8158	$\Delta H_{\text{calc}} = (0.853 \pm 0.166)^* \Delta H_{\text{exp}} + (6.351 \pm 11.233)$

Table 4. Average absolute errors, squares of correlation coefficients, and equations for correlations (without data point corresponding to trimethylphosphine) between experimental (ΔH_{exp}) and calculated (ΔH_{calc}) complexation energies between Lewis bases and BF_3 . All values are in kJ/mol

	Average absolute errors	Squares of correlation coefficient R^2	Correlation equation
HF/6-311+G**	19.7	0.8733	$\Delta H_{\text{calc}} = (0.913 \pm 0.156)^* \Delta H_{\text{exp}} + (14.380 \pm 10.284)$
B3LYP/6-311+G**	12.0	0.9374	$\Delta H_{\text{calc}} = (0.815 \pm 0.094)^* \Delta H_{\text{exp}} + (-1.301 \pm 6.226)$
MP2/6-311+G**	14.0	0.9006	$\Delta H_{\text{calc}} = (1.017 \pm 0.151)^* \Delta H_{\text{exp}} + (-12.671 \pm 9.989)$
MP2/6-311+G(2df,2pd)	10.9	0.9291	$\Delta H_{\text{calc}} = (1.014 \pm 0.125)^* \Delta H_{\text{exp}} + (-10.045 \pm 8.280)$
G2MP2	11.4	0.9254	$\Delta H_{\text{calc}} = (1.002 \pm 0.127)^* \Delta H_{\text{exp}} + (-11.315 \pm 8.412)$
CBS-QB3	10.0	0.9329	$\Delta H_{\text{calc}} = (1.026 \pm 0.123)^* \Delta H_{\text{exp}} + (-8.360 \pm 8.138)$

Table 5. Average absolute errors, squares of correlation coefficients, and equations for correlations (without data point corresponding to trimethylphosphine) between experimental (ΔH_{exp}) and calculated (ΔH_{calc}) complexation energies (including BSSE) between Lewis bases and BF_3 . All values are in kJ/mol

	Average absolute errors	Squares of correlation coefficient R^2	Correlation equation
HF/6-311+G**	31.3	0.8632	$\Delta H_{\text{calc}} = (0.879 \pm 0.156)^* \Delta H_{\text{exp}} + (23.846 \pm 10.344)$
B3LYP/6-311+G**	19.0	0.9152	$\Delta H_{\text{calc}} = (0.790 \pm 0.108)^* \Delta H_{\text{exp}} + (6.011 \pm 7.108)$
MP2/6-311+G**	23.4	0.8935	$\Delta H_{\text{calc}} = (0.929 \pm 0.143)^* \Delta H_{\text{exp}} + (19.095 \pm 9.484)$
MP2/6-311+G(2df,2pd)	13.3	0.9207	$\Delta H_{\text{calc}} = (0.931 \pm 0.122)^* \Delta H_{\text{exp}} + (8.405 \pm 8.077)$

Based on these results we are tempted to doubt in the experimental complexation enthalpy of trimethylphosphine. However, the correlation of all used gas-phase complexation enthalpies with those measured by Maria & Gal [13] in dichloromethane (see Fig. 3) suggests that trimethylphosphine indeed should have the reported complexation energy 79.1 kJ/mol with BF_3 . The reasons for this discrepancy between experiment and calculations need further investigation. Perhaps the W1 calculations could shed some light on that problem, but were prohibitively expensive for us at the moment. It would also be desirable to compare calculated and measured complexation energies for other phosphorous bases, but the lack of experimental data in the gas phase makes it impossible.

Comparison of the MP2 results obtained with two basis sets (6-311+G** and 6-311+G(2df,2pd)) indicates that additional polarization functions do not improve the correlation. On the contrary, in all cases (with or without inclusion of trimethylphosphine and with or without BSSE correction) the smaller basis set

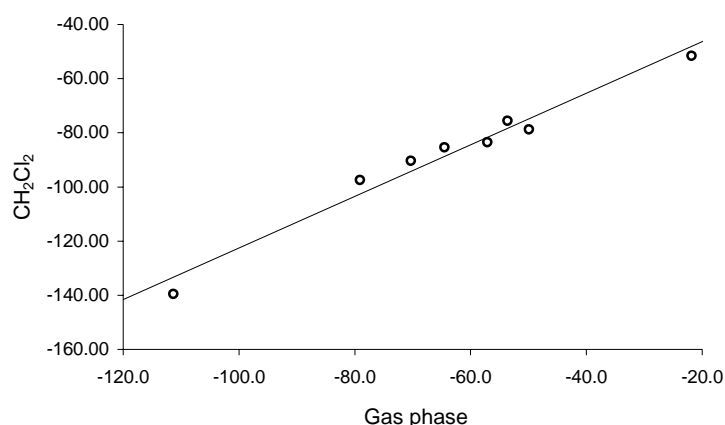


Fig. 3. Correlation between experimental complexation energies obtained in the gas phase and solution (dichloromethane).

gives better correlation as indicated by the somewhat larger R^2 values. However, the systematic errors are always somewhat smaller with the larger basis set as indicated by the slopes closer to unity and intercepts much closer to zero. So it seems that the better correlations obtained with the smaller basis set are the results of fortuitous cancellation of some errors and inclusion of larger systematic errors.

CONCLUSIONS

We have compared the ability of the HF, B3LYP, MP2, G2(MP2), and CBS-QB3 methods to predict the gas-phase complexation enthalpies of eight Lewis bases with borontrifluoride. The best results were obtained with the CBS-QB3 and MP2/6-311+G(2df,2pd) methods, without correction for BSSE. However, all calculations (except for HF and B3LYP) overestimated the gas-phase complexation enthalpies. Application of the BSSE correction by the counterpoise method overcorrected the error and gave systematically too low complexation energies.

The data point corresponding to trimethylphosphine systematically deviated from the correlation lines between calculated and experimental enthalpies. However, comparison with solution data did not permit to cast it away.

B3LYP/6-311+G** calculations seem to be best suited for investigation of trends in BF_3 affinities of different bases in the sense of compromise between speed and accuracy, while CBS-QB3 can be recommended for accurate calculation at absolute complexation energies between BF_3 and Lewis bases.

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Komplekseerumisentalpiad Lewisi aluste ja BF_3 vahel: mõnede arvutuskeemia meetodite võrdlus

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Kaheksa Lewisi aluse – dimetüüleetri, dietüüleetri, etüülatsetaadi, trimetüülamiini, trimetüülfosfiini, tetrahüdropüraani, tetrahüdrofuraani ja tetrahüdrotiofeeni – komplekseerumisentalpiad boortrifluoriidiga arvutati meetoditega HF/6-311+G**, B3LYP/6-311+G**, MP2/6-311+G**, MP2/6-311+G(2df,2pd), G2(MP2) ning CBS-QB3 ja võrreldi eksperimentaalselt leitud entalpiatega. Parim kokkulangevus eksperimendiga saadi CBS-QB3-meetodiga. Baasi superpositsioonivea korrigeerimine ülehindas viga ja andis tulemusena süstemaatiliselt liiga väikesed komplekseerumisentalpiad.

Ökonoomseim meetod suhtelise BF_3 afiinsuse arvutamiseks oli B3LYP/6-311+G**, mis annab aga suhteliselt suure süstemaatilise vea. Seetõttu on absoluutsete afiinsuste arvutamiseks eelistatud CBS-QB3-meetod.