Enthalpies of adduct formation between boron trifluoride and selected organic bases in solution: Toward an accurate theoretical entry to Lewis basicity

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Abstract： The Lewis basicity of selected organic bases, modeled by the enthalpies of adduct formation between gaseous BF_3 and the bases in dichloromethane (DCM) solution, is critically examined. Although experimental enthalpies for a large number of molecules have been reported in the literature, it may be desirable to estimate missing or uncertain data for important Lewis bases. We have decided to use high-level ab initio procedures, combined with a polarized continuum solvation model, in which the solvated species are the clusters formed by specific hydrogen bonding of DCM with the Lewis base and the Lewis base/BF_3 adduct. This mode of interaction with DCM corresponds to a specific solvation model (SSM). The results actually show that the enthalpy of BF_3 adduct formation in DCM solution is clearly influenced by specific interactions, DCM acting as hydrogen-bonding donor (HBD) molecule in two ways: base/DCM and adduct/DCM, confirming that specific solvation is an important contribution to experimentally determined Lewis basicity scales. This analysis allows us to conclude that there are reasons to suspect some gas-phase values to be in error by more than the stated experimental uncertainty. Some experimental values in DCM solution that were uncertain because of identified reasons can be complemented by the computed values.

Keywords: BF_3 enthalpies; Lewis basicity; Specific solvation; High-level ab initio calculations; Dichloromethane; Boron trifluoride

1. Introduction

The quantitative characterization of the Lewis basicity of a molecule or a functional group in a complex system is frequently a prerequisite for understanding the Lewis acid/base interactions which are pivotal in many fundamental and applied fields. The IUPAC definition of Lewis basicity as the "thermodynamic tendency of a substance to act as a Lewis base" is fundamentally correct, but, for practical realization, was primarily measured either as Gibbs energies or enthalpies of adduct formation relative to a standard Lewis acid, in the gas phase or in an inert (or supposed so) solvent [1-9].

Basicity is a multidimensional property [10-12], but characterization of an interaction with a multiparametric model is rather complex and requires an extended set of carefully chosen data.

For these reasons, the use of unidimensional scales (using a single reference Lewis acid) is often preferred, for example by looking at a simple linear regression. There are several, critically evaluated, Lewis basicity scales, covering a respectable range of bases [5]. These scales deal with the most useful interactions, like adduct formation with classical Lewis acids (in particular $SbCl_5$ and BF_3), hydrogen bonding, halogen bonding and gas-phase metal cation affinities. In fact, one of the most cited Lewis basicity scales is the so-called "Donor Number" (DN) due to Viktor Gutmann and his followers [13,14]. DN

was initially defined as the calorimetric measurement of the enthalpy of adduct formation between $SbCl_5$ and a Lewis base (LB) both dissolved in 1,2-dichloroethane (DCE).

$$SbCl_{5(DCE)} + LB_{(DCE)} \rightarrow [LB\text{-}SbCl_5]_{(DCE)} \qquad (1)$$
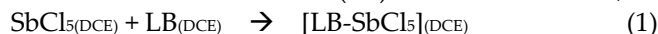
Despite various drawbacks, due in particular to experimental problems [5], the use of secondary, non-calorimetric, measurements to expand the scale, and traceability of the data [15], the DN scale is still cited as a fundamental reference in state-of-the-art research on materials [16-24], to cite only a few recent works.

Using a similar calorimetric definition, two of us established a Lewis basicity scale founded on the enthalpies of reaction between gaseous BF_3 and a Lewis base in dichloromethane (DCM) solution [5,25]:

$$BF_{3(gas)} + LB_{(DCM)} \rightarrow [LB\text{-}BF_3]_{(DCM)} \qquad (2a)$$
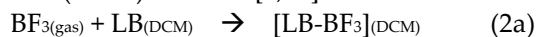
Some measurements were also carried out in nitrobenzene (NB) solution:

$$BF_{3(gas)} + LB_{(NB)} \rightarrow [LB\text{-}BF_3]_{(NB)} \qquad (2b)$$

This $\Delta H BF_3$ scale (BF$_3$A in ref 5 where A was used by analogy with PA, the proton affinity measured by an enthalpy) presents several advantages over DN, particularly by the range of enthalpies covered, obtained by a single technique, the wide structural variation among the LBs, its rigorous traceability from the same laboratory, including repeatability tests of calorimetric measurements [26].

Actually, the DN and $\Delta H BF_3$ scales are strongly correlated [5,25], within the range of O- and N-bases for which data are available.

Owing to the need of data for the Lewis basicity of molecules not experimentally characterized [27], several attempts were recently made for the estimation of either $SbCl_5$ or BF_3 enthalpies of adduct formation by quantum chemistry methods, see for example [22,28-30].

We also contributed to the evaluation of high-level theoretical methods for calculating the enthalpies for reactions (1) and (2) [31].

There are also data corresponding to BF_3 enthalpies experimentally determined in the gas phase:

$$BF_{3(gas)} + LB_{(gas)} \rightarrow [LB\text{-}BF_3]_{(gas)} \qquad (3)$$
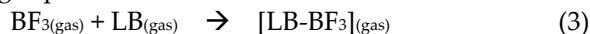
In this work, we investigate the best available ab initio methods, compatible with the size of the adducts, to calculate BF_3 enthalpies of adduct formation, reactions (2) and (3). In the case of reaction (2), we chose a series of representative Lewis bases covering the maximum span of the $\Delta H BF_3$ scale. Examination of reaction (3) was limited to the data available in the literature.

The energetics associated with the interaction of the different bases under study with BF_3 have been investigated using a G4* ab initio method that is described in detail in the Computational section. Our aim was to determine how close we can come to the experimental enthalpies of adduct formation, in the gas phase and in solution. For measurements in DCM solution, $\Delta H BF_3$, for which there is a large choice of experimental data [5], the examination of models of solvent effects was believed to be essential.

From the definitions of DN and $\Delta H BF_3$ following reactions (1) and (2) respectively, the two Lewis basicity scales correspond to Lewis bases and their adducts as solutes diluted in a given solvent (solute scales). This point is often overlooked, and these scales are very frequently considered as solvent scales, leading one to believe that interactions between solvent and solute molecules are only considered in terms of Lewis acid/Lewis base binding [32-34]. This approximation may be an acceptable approximation for weakly associated liquids used as solvents, but is certainly not valid for self-associated liquids [35].

2. Results and Discussion

2.1. Gas phase enthalpies

As a prerequisite for potential comparisons between theoretical and experimental enthalpies of BF_3 adduct formation with bases and adducts in solution (reaction 2), an exploratory analysis of gas-phase data was conducted on seven selected Lewis bases. As the reaction of adduct formation with BF_3 is always exothermic (negative values), we systematically list and discuss $-\Delta H$ values for convenience. The enthalpies are calculated at a

slightly modified G4 level, described in the computational section, and from now we label this procedure G4*, to make a distinction from the standard G4 method. The experimental and calculated enthalpies of reaction (3) at the G4* level are listed in Table 1. The B3LYP/aug-cc-pVTZ optimized geometries of the BF$_3$ complexes in the gas phase are given in Table S4 of the Supporting Information.

Table 1. Gas-phase enthalpies ($-\Delta H$) of adduct formation with Lewis bases; values in kJ·mol^{-1} at 298 K unless otherwise noted.

Lewis base	G4*-Calculated [a]	Experimental	Δ(Calc.-Exp.)
Trimethylamine	126.4	111.3 ± 8.4 [b] [36-38]	15.1
Dimethyl ether	62.4	57.1 ± 0.8 [39]	5.3
Tetrahydrofuran	72.5	70.3 ± 0.8 [40]	2.2
Tetrahydropyran	69.0	64.5 ± 0.8 [40]	4.5
Ethyl acetate	55.9	53.6±2.9 [41]	2.3
Trimethylphosphine	66.1	79.1 [42,43]	-13.0
Tetrahydrothiophene	37.9	21.8 ± 1.7 [44]	16.1

[a] see text and computational section; [b] at 273 K.

The calculated values are in fair agreement for the O-bases, but rather significant deviations are observed for the N-, S-, and P-bases. It should be noted that most of these experimental enthalpies were obtained by tensimetric measurements of the dissociation of the gas-phase adducts at different temperatures, which are subject to systematic errors, in particular for the early studies [45].

The gas-phase trimethylamine experimental enthalpy listed in Table 1 was estimated from a thermochemical cycle involving conjectured quantities for both the enthalpy of formation of the solid trimethylamine/boron trifluoride adduct (42 ± 2 kcal·mol^{-1}) and for its enthalpy of sublimation (15 kcal·mol^{-1}) [38]; a higher reported value (68.9 kJ·mol^{-1} at 393K) [46] worsen the deviation between calculated and experimental values. So, the often-quoted value reported in Table 1 appears to be a rough estimate, and the calculated value is probably a better approximation of the true one. As a matter of fact, the G4 calculated proton affinity (PA) of trimethylamine (950.4 kJ·mol^{-1}) is in very good agreement with the experimental value (948.9 kJ·mol^{-1}) [47], showing that the G4 method reproduces very well the enthalpies of both the neutral trimethylamine and its protonated form, and it is not likely that it overestimates the stability of the trimethylamine/BF$_3$ adduct. The good agreement between the experimental PAs and the G4-calculated values is also observed for all the other Lewis bases included in this study, as shown in Table S3 of the Supporting Information.

For the tetrahydrothiophene/BF$_3$ adduct [44], the authors report some decomposition during the vaporization of the solid adduct. In this case, the G4 calculated PA (848.7 kJ·mol^{-1}) is again in excellent agreement with the experimental value (849.1 kJ·mol^{-1}) [47], which leads us to believe that the theoretical estimate for the enthalpy of formation of the tetrahydrothiophene/BF$_3$ adduct is probably the closest to the correct value. A similar decomposition problem is reported for the trimethyl phosphine/BF$_3$ adduct [43], for which the theoretical estimate, as it was the case for trimethylamine, is significantly larger than the experimental value, whose cited source of data [48] is difficult to trace.

To summarize, there are reasons to suspect some gas-phase values to be in error by more than the stated experimental uncertainty.

It is also interesting to mention that in principle one could think naively that the basicity of the compounds included in our analysis with respect to BF$_3$ should follow the same trends as their intrinsic (gas-phase) Brønsted basicity, i.e., the trend exhibited by the gas-phase proton affinities. This is indeed the case when dimethyl ether is compared with tetrahydrofuran and tetrahydropyran. Dimethyl ether exhibits a BF$_3$ enthalpy smaller than tetrahydrofuran and tetrahydropyran, as it is the case for their intrinsic Brønsted basicities (PAs), 792.0 kJ·mol^{-1} for dimethyl ether, and 822.1 and 822.8 kJ·mol^{-1} [47], respectively, for tetrahydrofuran and tetrahydropyran. This result seems to be consistent, as

shown in Figure 1, with the electron densities at the corresponding B-O bond critical points (BCPs), being lower for dimethyl ether/BF₃ complex than for the complexes involving tetrahydrofuran and tetrahydropyran. Also consistently, the Wiberg bond order obtained in the framework of the NBO approach for the B-O interaction is also smaller for the dimethyl ether/BF₃ complex (0.377) than for the tetrahydrofuran/BF₃ and tetrahydropyran/BF₃ ones (0.386 and 0.398, respectively). However, if we consider the couple tetrahydrofuran and tetrahydropyran, we observed that whereas their PAs are practically equal, as mentioned above, the BF₃ affinity of tetrahydrofuran is clearly larger (both the theoretical estimates and the experimental measurements) than that of tetrahydropyran. More significant are the changes when looking at the values associated to ethyl acetate. Both, the calculated and the experimental BF₃ affinities for ethyl acetate are the lowest of the four oxygen bases included in Table 1, whereas its proton affinity (835.7 kJ·mol⁻¹) is the largest of the series. These results are in line with those reported by A. Rauk et al. [49] based on MP2 ab initio calculations.

It must be ratified then, that no correlation should be expected between BF₃ interaction enthalpies and proton affinities. As a matter of fact, protonation is a very different process, in which the attachment of a proton to the basic site of the base implies a huge charge transfer from the base, with a concomitant strong polarization of its charge density, to the incoming proton, resulting in the formation of a new covalent bond between the basic site and the proton. On top of that, another important difference between the protonation process and the formation of BF₃ complexes, is the possibility, in the last case, of having also non-covalent interactions between the fluorine atoms of BF₃ with other atoms of the base, which are not possible in protonation processes. This is quite evident when looking at the molecular graph of the ethyl acetate/BF₃ complex, which shows the formation of C-H···F hydrogen bonds between the C-H bonds of the base and the BF₃ fluorine atoms. The formation of these hydrogen bonds is also corroborated by the NBO analysis which shows a non-negligible population of the corresponding C-H antibonding orbitals, resulting in a lengthening of 0.006 Å (1 Å = 100 pm) of the two C-H bonds involved, and in a decrease of the electron density at the C-H BCP (see Figure 1).
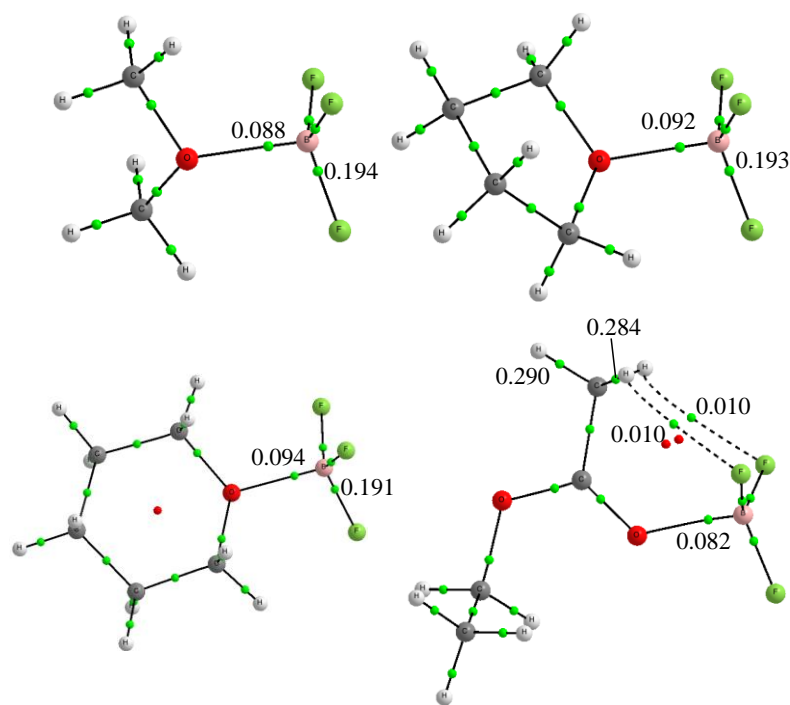
Figure 1. Molecular graphs for the complexes between dimethyl ether, tetrahydrofuran, tetrahydropyran and ethyl acetate with BF₃. The green dots show the positions of the bond critical points, whose electron density in a.u. is indicated for relevant cases.

2.1. Enthalpies in solution

From the very large ΔHBF$_3$ data set measured in DCM [5,10,25,31], we have selected a series of Lewis bases which partly overlap the experimental gas-phase enthalpies of reaction (3), and covers the largest possible range of Lewis basicities, with a wide variation of functional groups. The selection includes quinuclidine, one of the strongest bases (150 kJ·mol^{-1}) in this solute scale, and nitrobenzene (acting as a Lewis base, 36 kJ·mol^{-1}) as the weakest.

Some BF$_3$ enthalpies were also measured in nitrobenzene as solvent [25], to check the medium effect, but also for solubility problems, or because secondary reactions between DCM and some bases or their adducts plagued calorimetric measurements. The experimental data are listed in Table 2. The listed uncertainties, defined as the 95% confidence interval, correspond to the short-term repeatability. Systematic errors, discussed in detail in Materials and Methods, may add about 1 to 2 kJ·mol^{-1} to the listed uncertainties.

Several experimental data were unpublished, so the experimental method [26] is briefly recalled in the Materials and Methods section.

For a series of 12 well-behaved Lewis bases, a linear least square regression between the BF$_3$ enthalpies in the two solvents (dichloromethane and nitrobenzene) leads to equation (4) (coefficient of determination $R^2 = 0.9940$; units kJ·mol^{-1}) [25].

$$-\Delta H_{\text{(DCM solution)}} = 0.958 \, [-\Delta H_{\text{(NB solution)}}] - 0.31 \qquad (4)$$

As explained in Materials and Methods, amines may be subject to secondary reactions in DCM. This is the origin of the higher-than-usual uncertainty of the enthalpy value for quinuclidine in DCM. For this reason, the enthalpy value is estimated using equation (4) as well. This equation is also applied to the enthalpy of solution of BF$_3$ in nitrobenzene, considered as a Lewis base in nitrobenzene solution, leading to an estimation of the enthalpy in DCM.

Table 2 also gives the ab initio calculated enthalpies in DCM and NB solution, and in the gas phase for comparison. Our objective was to reproduce the most accurately possible the absolute enthalpies of BF$_3$ adduct formation in solution, equation (2). Previously, we applied the polarized continuum model (PCM) to calculated enthalpy values, using the standard G4 method, for 8 phosphoryl bases [31], and compared with experimentally available data. Although the results were promising, the enthalpies calculated in the two solvents were quite close, with maximum differences of about 2 kJ·mol^{-1} for values in the range 27 to 129 kJ·mol^{-1}. This result is not completely consistent with equation (4), which indicates that enthalpies in DCM should be about 96% of those in NB. The continuous solvation model for DCM was applied to 12 Lewis bases pertaining to the present study, and the results are given in Table S1 of the Supporting Information. The calculated values are almost always too high as compared to the experimental ones. A part of this discrepancy was attributed to a specific solvent effect of DCM, which is known to be a weak hydrogen bond donor (HBD) [50-54]. It may be considered that the interactions of DCM with the bases and BF$_3$ adducts are primarily dipole/dipole, but the structure of the interacting species (Figure 2) indicates an enhancement by directional hydrogen bonding, through the appropriate orientation of the DCM molecule.

It may be argued that halogen bonding may be additionally involved in DCM/Lewis base interaction, but solid phase studies show that hydrogen bonding is dominant for F, O, N, S and P-bases, while it competes with halogen bonding for Cl, Br, or I.-bases [55]. Therefore, we can conclude that in our case, H-bonding is the most significant non-specific solvation in DCM solution.

The enthalpy of BF$_3$ adduct formation may be influenced by specific interactions with DCM acting as HBD molecule in two ways: base/DCM and adduct/DCM. Reaction (2) corresponds to the addition of gaseous BF$_3$ to a Lewis base solution, so H-bonding to the isolated BF$_3$ is not relevant here. The specific solvation of Lewis bases by DCM was suggested by Drago and coworkers [51], and a correction to the BF$_3$ enthalpies for DCM solvation was proposed [52]. Although several modes of H-bonding may be expected for the interaction Lewis base/DCM or BF$_3$ adduct/DCM, we opted for the simple model: one H-bond with the electron lone pair of the Lewis base, and three H-bonds (one on each fluorine of coordinated BF$_3$) for the adduct. Figure 2 shows two typical cases of calculated

structures of the solutes in reaction (2a) interacting by H-bonding with DCM. In addition to the specific solvation characterized by the Lewis base/DCM and by the adduct/DCM interactions, the PCM model was applied to these H-bonded systems to allow for the non-specific solvation.
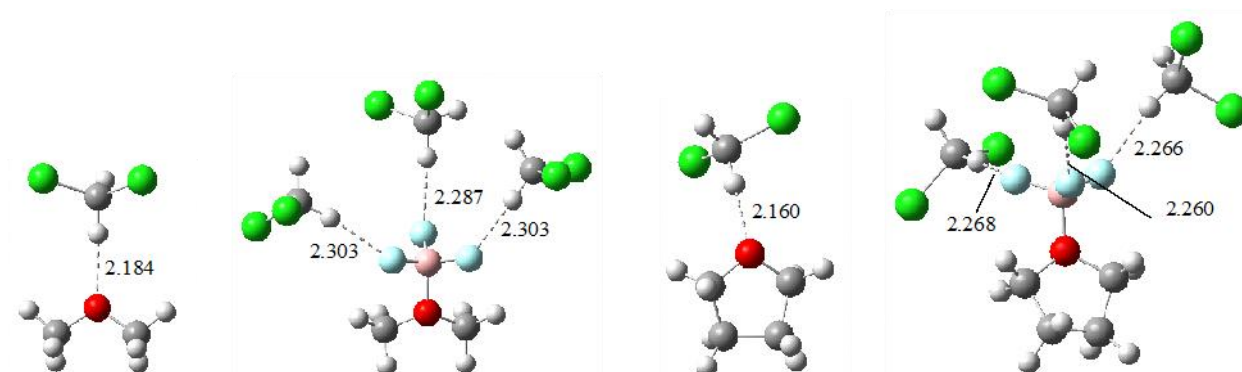
Figure 2. Examples of B3LYP/6.31+G(d,p) optimized structures of hydrogen bonded species which were considered for the specific solvation effect by DCM for dimethyl ether and tetrahydrofuran as suitable example. Before adduct formation, the Lewis base is in interaction with one DCM molecule. On the other hand, the BF$_3$ adduct is in interaction with three DCM molecules through the three fluorine atoms. H-Bond distances in Å.

Other arrangements with two H-bonds between the basic site and the DCM molecule were higher in energy and frequently we did not find minima but rather saddle points. Two paradigmatic examples are shown in Figure 3.
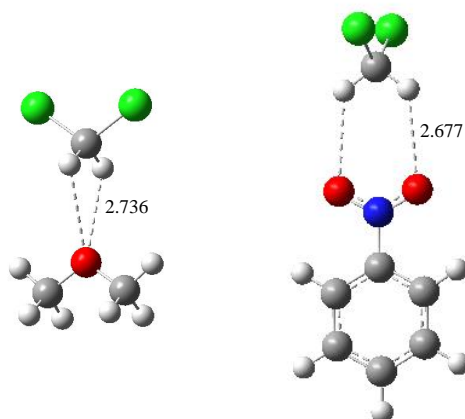
Figure 3. Stable structures for the solvation complexes between dimethyl ether and nitrobenzene with DCM stabilized by two H-bonds. Any of them are local minima of the potential energy surface but saddle points with two imaginary frequencies. Hydrogen bond distances in Å.

Solvation by nitrobenzene was considered as essentially due to non-specific interaction, and the PCM model was directly applied. In Table 2, we can see that most calculated values at the G4*/specific solvation model (SSM) are within ± 6 kJ·mol^{-1} (mean unsigned deviation = 4.2 kJ·mol^{-1}) of the experimental values for reaction (2a). There are two exceptions to this fit, quinuclidine and HMPA. Quinuclidine presents some experimental problem for measurements in DCM, explaining the larger-than-usual uncertainty. For this reason, the enthalpy was also measured in NB, and an estimation of the enthalpy in DCM was obtained using equation (4), showing a better agreement with the calculated values, although still away by 9.5 kJ·mol^{-1}. The second exception is HMPA. Our simplified SSM considers only one H-bond on the basic center of the Lewis base, the phosphoryl oxygen atom, but the three nitrogen atoms of the dimethylamino groups are also potential basic site, although weaker than the phosphoryl. The cluster corresponding to more than one DCM molecules bound to HMPA is not amenable to G4 calculations and the hypothesis of an additional specific solvation on the nitrogen sites of HMPA could not be tested.

Overall, the SSM + PCM solvation scheme appear to perform satisfactorily for reproducing the enthalpies of adduct formation with BF_3 for the N-, O-, P- and S-bases studied.

The success of PCM solvation applied to the measurements conducted in nitrobenzene as solvent is mitigated. The calculated $-\Delta H$ values for the six cases in Table 2 are almost all too large, with disagreements with experimental enthalpies up to 12 kJ·mol^{-1}. It should be noted, as far as the calculations are concerned, that our theoretical treatment includes a geometry optimization of the complex when solvent effects are accounted for. Curiously, for HPMA, these values are in worse agreement with the experimental ones than those obtained when no geometry optimization of the complex is carried out. Provisionally, we assign this observation to the neglect of the potential solvation of the NMe_2 groups of HMPA in the SSM.

We would like to point out that the high computational level required to reproduce $\Delta H BF_3$ values is not attainable for DN (i.e., enthalpies of adduct formation with $SbCl_5$ in solution). This is a further advantage of using $\Delta H BF_3$ as a Lewis basicity scale, by widening the possibilities of evaluating this kind of basicity for species other than those already experimentally characterized by calorimetry [5].

Table 2. Experimental and calculated enthalpies of adduct formation ($-\Delta H$, kJ·mol^{-1} at 298 K)) between BF$_3$ and Lewis bases in dichloromethane (DCM) and nitrobenzene (NB) solutions (reactions (2a) and 2b); kJ·mol^{-1}). The signification of uncertainties on experimental enthalpies is discussed in the text. G4*-calculated gas-phase enthalpies are listed in the last column.

Lewis base	Solvent CH₂Cl₂ (DCM)			Solvent PhNO₂ (NB)			Gas phase
	Experimental in DCM [a]	G4* + discrete solvation model [b]	Δ = calc - exp	Experimental in NB [a]	G4* + continuous solvation model [c]	Δ = calc - exp	G4*
Trimethylamine	139.5 ± 1.8	145.7	6.2				126.4 [e]
N-Methylpyrrolidine	139.5 ± 0.8	143.8	4.3				125.2
Quinuclidine	150.01 ± 3.48 [153.4 ± 0.9] [d]	162.9	12.9 [9.5]	160.5 ± 0.9	171.2	10.7	139.1
Pyridine	128.1 ± 0.5	126.3	-1.8	137.9 ± 0.7	137.4	-0.5	100.4 [e]
Acetonitrile	60.4 ±0.5	60.7	-0.3				32.3
Dimethyl ether	83.6 ± 0.2	78.0	-5.6				62.4
Tetrahydrofuran	90.4 ± 0.3	96.2	5.8	93.0 ± 0.3	103.9	10.9	74.8
Tetrahydropyran	85.4 ± 0.5	81.2	-4.2				69.0 [e]
Acetone	76.0 ± 0.2	74.3	-1.7	78.1 ± 0.3	82.7	4.6	54.2
Ethyl acetate	75.6 ± 0.3	73.2	-2.4				55.9
γ-Butyrolactone	75.1 ± 1.2	71.7	-3.4				53.1
Dimethyl carbonate	67.6 ± 0.4	62.8	-4.8				30.8
Nitrobenzene	[35.8 ± 1.4] [d,f]	39.3	[3.5]	37.7 ± 1.4 [g]	45.3	7.6	21.0 [e]
Hexamethyl-phosphoramide (HMPA)	117.5 ± 0.5	127.7	10.2	123.1 ± 0.5	135.2 (121.9) [i]	12.1 (-1.2)	101.3 [h]
Trimethylphosphine	97.4 ± 0.3	97.5	0.1				66.1
Tetrahydrothiophene	51.6 ± 0.2	54.8	3.2				37.9

[a] Experimental values corresponding to the reaction: BF₃(gas) + LB(solution) → [LB-BF₃](solution).

[b] Solvation effects are calculated using a model combining specific interactions (SSM) and a continuum model; see text.

[c] Solvation effects are calculated using a continuum model, including geometry optimization at the B3LYP/6-31+g(d,p) level of theory.

[d] Secondary value calculated from measurements in NB [25]. The assigned uncertainty corresponds to the repeatability, see text, but additional uncertainties are expected by converting to a value in DCM as solvent.

[e] In these particular cases, the standard G4 yields a higher value than the one obtained with the non-standard G4* procedure; see Table S2.

[f] Value for the Lewis base PhNO₂ in CH₂Cl₂ solution, estimated using equation (4), see text.

[g] Value measured for the dissolution of BF₃ in pure PhNO₂, corresponding to the adduct formation with the Lewis base PhNO₂ in PhNO₂ solution.

[h] Published value obtained by extrapolation of the G4MP2 results [31].

[i] Solvation effects do not include geometry optimization. The previously reported value (119.3 kJ·mol^{-1}) [31] is very close but not strictly equal because the basis set used in the calculation of the solvation effects was different from the one used here.

Finally, it is worth mention, that as illustrated in Figure 4, there is a rather good linear correlation between the experimental enthalpies $\Delta H BF_3$ in DCM solution and the G4* calculated values obtained using the discrete solvation model (SSM). This linear correlation obeys the equation:

$-\Delta H BF_{3calc.} = 1.078 (-\Delta H BF_{3exp.DCM}) - 5.900$; $R^2 = 0.985$
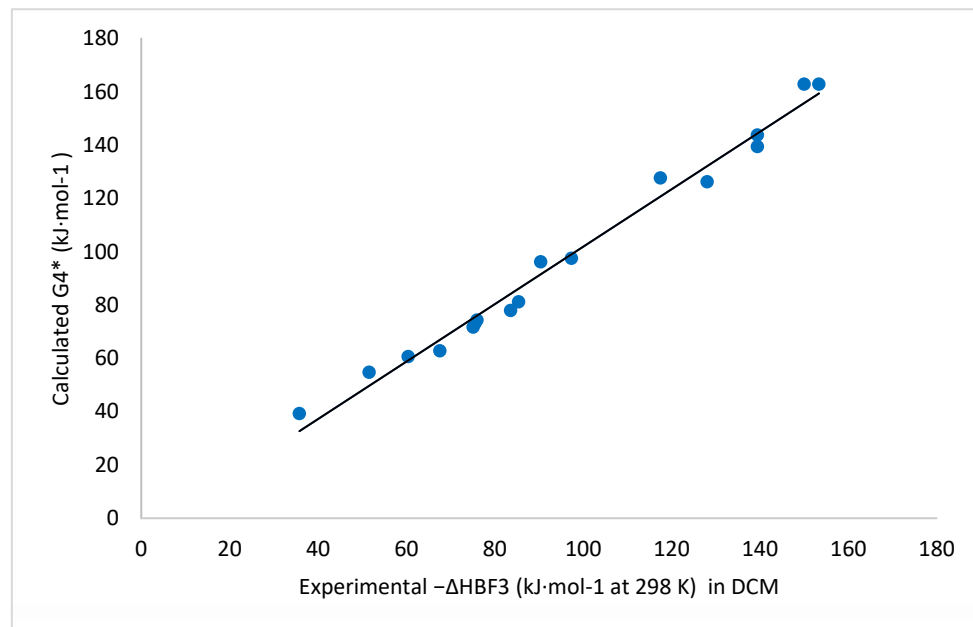
Figure 4. Linear correlation between the experimental enthalpies of adduct formation ($-\Delta H BF_{3exp.DCM}$) and the G4* calculated values obtained using the discrete solvation model.

4. Materials and Methods

4.1. Calorimetric method

We succinctly recall the essential of the calorimetric method utilized for our enthalpy measurements [26]. The calorimeter was a Tian-Calvet differential microcalorimeter, with two 17 mm diameter cells. The measuring and reference cells were made of borosilicate glass. All measurements were done at 25.0 ± 0.1 °C, under ambient atmospheric pressure. The system was calibrated by Joule effect, giving uncertainties on the calorimeter calibration constant much less than 0.1% (short time precision at the 95% confidence level for a series of more than 10 measurements), and about 0.5% for the long-term accuracy (drift of the constant over 5 years). The BF_3 quantity injected in the Lewis base solution was measured by a mercury manometer (PVT measurements) in a constant temperature room at 20.0 ± 0.1°C. The repeatability of the enthalpies reported in Table 2 (usual range 0.5-1% for about 10 consecutive measurements on the same solution) are largely due to errors on the BF_3 measurements. The long-term reproducibility (several years) of the calibration constant was better than 0.5% when considering the drift of the calibration constant. Systematic errors come also from measurements of gas quantities, which were evaluated as about 0.2% [26]. Our calorimetric measurements give absolute enthalpies of reaction measured consistently using the same protocol. If we compare our data with those measured by H. C. Brown and coworkers for 5 Lewis bases in NB solution, using a different calorimetric procedure, we observe a fair to excellent agreement [25], showing that systematic errors on our enthalpies are less than 1%.

In some cases, we had to consider larger than usual errors on the heat effect, because of secondary reactions. The amines have tendencies to react with methylene chloride but to very different degrees [51,56]. For trimethylamine and N-methylpyrrolidine, we did not observe significant reaction DCM/amine or DCM/adduct, but quinuclidine displayed this problem. This DCM/quinuclidine concentration-dependent reaction was already

observed by Drago et al. [51]. The larger uncertainty on the enthalpy of adduct formation in DCM for this compound was imputed to such problem.

4.2. Computational

The G4* approach used in our calculations is a slight modification of the G4 ab initio method [57]. The G4 theory is a composite formalism based on the use of Moller-Plesset perturbation theory up to fourth order and CCSD(T) coupled cluster theory to accurately describe electron correlation effects. The method includes a final correction for the Hartree-Fock limit evaluated using an extrapolation procedure and quadruple-zeta and quintuple-zeta basis sets. It must be mentioned however that in this study we have introduced a slight modification as far as the optimized geometries are concerned. Indeed, since in our case we are dealing with rather weak interactions which usually required the use of diffuse functions which are not included in the standard G4 formalism, which uses B3LYP/6-31G(2df,p) optimized geometries, we have decided to use a B3LYP/aug-cc-pVTZ optimized geometries (see Table S4 of the Supporting Information) instead of the standard B3LYP/6-31G(2f,p) ones. These slightly modified G4 calculations are named as G4* elsewhere.

To analyze the bonding characteristics of some of the complexes under investigation chosen as suitable illustrations, we have used two different approaches, namely the atoms in molecules (AIM) method [58] and the Natural Bond Orbital (NBO) approach [59].

The AIM formalism permits to locate the so-called bond critical points (BCPs) and calculate the corresponding electron density, whose value at the BCPs is a good measure of the strength of the linkage and also provides information about its covalent character, through the values and sign of the Laplacian and the energy density. The NBO method provides, through an appropriate molecular orbital localization scheme, a description of the systems in terms of a Lewis type representation. When dealing with intermolecular interactions this approach is very well suited to estimate the relative strength of the interaction between the groups involved.

To account for solvation effects, we have used semi-continuum or cluster-continuum approaches [60]. Often used in the context of solvation of ions by water, these approaches are supposed to complete the electrostatic description of the polarized continuum model (PCM) developed by Tomasi et al. [61]. In the model, the continuum approaches are used on clusters in which the molecule and its adduct with BF_3 are specifically solvated by one and three molecules of DCM, respectively. This increases notably the size of the systems to be investigated and therefore these calculations to account for the solvation stabilization effects have been carried out at the B3LYP/6-31+G(d,p) level of theory.

5. Conclusions

The experimental enthalpies of adduct formation between neutral Lewis bases and boron trifluoride measured in dichloromethane are available for about 350 molecules [5]. One of our objectives was the reproduction of absolute enthalpy values using the state-of-the-art ab initio approaches. A previous work on a series of phosphoryl compounds using G4 calculations and a continuous solvation model was rather successful, but application to the various bases included in the present work led us to conclude that the solvation model should be refined. Using an improved G4* combined with a solvation model including specific hydrogen bonding to the Lewis base and the BF_3 adduct, completed by a continuous solvation model (PCM), was more satisfactory for the reproduction of the experimental enthalpies in DCM.

Comparison of BF_3 enthalpies measured and calculated in the gas-phase and in DCM solution shows that the solvent effect is sizeable. The use of DCM for reaction (2a), like probably the use of DCE (1,2-dichloroethane) for reaction (1), was dictated by solubility problems, mainly for the BF_3 adducts, which are poorly soluble in low polarity solvents like tetrachloromethane and alkanes.

Solvation is an important component to Lewis basicity measurements. A recent computational study focused on Gibbs energies of adduct formation between antimony

pentahalides and group 13 Lewis acids (among them SbCl$_5$ and BF$_3$) and the Lewis bases acetonitrile and pyridine examined the solvent effect on the basis of a continuous dielectric model. The authors concluded that electrostatic, dispersion and electron-repulsive solute-solvent interactions are essential for the prediction of solvation effects [62], while the solvents selected for the study did not include possible hydrogen bond-donor solvents. It is worth mentioning that G4/G4* calculations are not currently possible for antimony pentahalide adducts, in particular for estimating DN, reaction (1).

Our hybrid discrete-continuum solvation model approach appears to be efficient for the selected Lewis bases. Most experimental ΔHBF$_3$ are reproduced within ±6 kJ mol^{-1}, opening the way to the theoretical evaluation of Lewis basicity, as defined by reaction (2a), in particular for molecules not experimentally characterized. At the cost of time-consuming and expensive computations, more sophisticated DCM/Lewis bases and DCM/BF$_3$ adducts may be devised, but for a more widespread applicability, it is probably advisable to search for less expensive methods.

The importance of solvent effects on Lewis basicity points out the necessity to distinguish between the Lewis basicity defined by reactions (1) and (2) and "solvent basicity". Solvent basicity is often an ill-defined property, considering only the experimental or computed thermochemistry of reactions (1)-(3), and ignoring the "bulk effect", i.e., the variable solvation of each solvent [35]. Further experimental and computational studies are planned on the Lewis basicity of solvents, as opposed to solute, i.e., the enthalpy of solution of BF$_3$ in bulk liquids.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1: S1. Calculated solvation effects on the enthalpies of BF$_3$ adduct formation; S2. Comparison of calculated gas-phase enthalpies: G4* vs. standard G4; S3. Comparison of experimental gas-phase PAs with G4-calculated values; S4. Optimized structures of the adducts formed between boron trifluoride and Lewis bases included in this study.

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