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B3LYP and MP2 Calculations of the Enthalpies of Hydrogen-Bonded Complexes of Methanol with Neutral Bases and Anions: Comparison with Experimental Data

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To perfect a method for building a theoretical hydrogen-bond basicity scale, the enthalpy of hydrogen bonding between methanol and thirteen neutral and anionic bases (MeOH, $MeNH_2$, Me_2NH, Et_2NH, Me_3N, Et_3N, Br^-, CN^-, SH^-, Cl^-, $HCOO^-$, MeO^-, F^-) was calculated by DFT and ab initio methods. The theoretical results were compared to selected experimental ones. It appears that B3LYP/6-31+G(d,p) calculations are satisfactory for optimizing the geometry of complexes and giving a general order of basicity. However, they are deficient for reproducing the large effect of alkyl groups on the hydrogen-bond basicity of amines. This deficiency is explained by intermolecular perturbation theory calculations, which show that the alkylation of nitrogen dramatically increases the dispersion energy component not taken into account by the B3LYP functional. Of the methods considered, only MP2/aug-cc-pVTZ calculations are capable of reproducing the binding enthalpy within the experimental error for the first-row acceptor atoms N, O, and F, and of accounting for dispersion effects created by alkylation at the hydrogen-bond acceptor site.

I. Introduction

In conventional hydrogen bonds, hydrogen-bond donors (HBDs) of chemical and biological interest are mostly confined to NH, OH, and CH groups.[1−3] In contrast, hydrogen-bond acceptors (HBAs) vary much more in character.[1−3] They correspond to many atoms of groups 15, 16, and 17,[4,5] which can be variously functionalized and substituted.[6] For example, the HBA strength of a nitrogen atom is expected to be different in nitriles, imines, diazo compounds, pyridines, or amines, and in ammonia and primary, secondary, and tertiary amines.

To understand the chemical, physical, and biological molecular properties that depend on hydrogen bonding, bench chemists have established scales of HBA strength of organic molecules, B, by measuring the Gibbs energy[7−10] or enthalpies[11−14] of reaction 1, in the gas

$$X-H + B \rightleftarrows X-H\cdots B \qquad (1)$$

phase[15] or in solution,[7−14] by selecting a reference HBD, X−H, e.g., 4-fluorophenol,[7,10,11,13,14] 4-nitrophenol,[8] cyclohexanol,[12] or 5-fluoroindole.[9] However, most of these measurements are limited to molecules with only one HBA site. In the case of the polyfunctional molecules most often encountered, the usual methods do not generally provide the individual HBA strength of each HBA site.[16−18] We have to turn to quantum chemistry methods in order to calculate these HBA strengths.[16−18]

The hydrogen bonding of a single HBD with a variety of organic molecules has been the subject of several computational studies in the past.[5,19−24] They differ in the choice of the reference HBD (HF,[5,23,24] H_2O,[19,20,22,23] and $4\text{-}FC_6H_4OH$[21]), the variety of HBAs, the level of theory (semiempirical,[21] Hartree−Fock,[19,22] density functional theory,[23,24] and correlated levels[5,20,23]), the computational strategy, the kind of energy calculated (dissociation energy D_0,[5,23] binding enthalpy ΔH_T,[19−22,24] or Gibbs energy ΔG_T[20,24]), and the method of comparison with experimental quantities.

The comparison with experimental energies is essential, since it identifies the level of theory that yields reliable energies at minimal computational expense. Unfortunately, it has not always been conducted quite satisfactorily. Indeed, comparisons have been made between energies calculated in vacuo and measured in CCl_4 solution,[19,21−24] despite the well-established influence of solvent on the thermodynamics of hydrogen bonding.[25−27] A second shortcoming arises from the comparison[19,22−24] of different HBDs in the calculations (HF or H_2O) and in the experiments ($4\text{-}FC_6H_4OH$).[28] Last, comparisons have been made between quantities that are different in character. For example, the calculated dissociation energy has also been correlated in the comprehensive reference[23] to the experimental gas-phase proton affinity.

This work builds on the earlier studies of H_2O, HF, and $4\text{-}FC_6H_4OH$ HBDs. Here, we have studied complexes with CH_3OH as an HBD, and we develop a clear and robust methodology for assessing various computational levels of theory. First, we have identified the available experimental gas-phase hydrogen-bond enthalpies for complexes involving methanol. Gas-phase results offer a more appropriate comparison with theory and avoid the necessity of modeling or approximating solvent effects. We have chosen to compare hydrogen-bond enthalpy rather than free energy to minimize the errors introduced by assuming harmonic vibrations in the complexes: anharmonicity can be important in loosely bound systems such as hydrogen bonds, and the harmonic approximation can, in particular, introduce large errors in entropy.[29] In this way, we obtain thirteen experimental enthalpy values for comparison, corresponding to six enthalpies for neutral complexes with methanol (with HBAs MeOH, $MeNH_2$, Me_2NH, Me_3N, Et_2NH, Et_3N) and seven for anionic complexes (with HBAs F^-, Cl^-, Br^-, CN^-, MeO^-, SH^-, and $HCOO^-$). The experimental hydrogen-bond enthalpies for

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TABLE 1: Experimental Binding Enthalpies at 298 K, $\Delta H°$(exp.), Deviation of Theoretical Enthalpies from Experiment, $\delta(\Delta H)$, and Mean Absolute Deviation, MAD (in kJ mol^{-1}) for the Hydrogen-Bonded Complexes of Methanol with a Variety of Acceptors, at the B3LYP and MP2 Levels Using Different Basis Sets[a]

		$\delta(\Delta H)$(theoretical−experimental)					
		B3LYP			MP2 (full)		MP2 (fc)
acceptors	$\Delta H°$(exp.)	6-31+G(d,p)	6-311+G(3df,2p)	aug-cc-pVTZ	6-311+G(3df,2p)	aug-cc-pVTZ	aug-cc-pVTZ
MeOH	−17.2 ± 2.1	2.5	4.6	4.6	1.9	1.2	1.2
$MeNH_2$	−23.4 ± 1.0	1.5	4.1	4.0	1.0	−0.1	−0.2
Me_2NH	−25.9 ± 1.0	4.5	7.1	6.9	1.6	0.5	0.3
Et_2HN	−28.0	6.9	9.2	9.1	0.4	−1.0	−1.2
Me_3N	−28.9 ± 1.0	6.3	8.8	8.7	0.8	−0.3	−0.5
Et_3N	−31.4 ± 2.0	15.1	17.4	16.5	2.7	1.1	0.6
Br^-	−60.7 ± 0.4	8.4	9.1	8.8	5.1	3.3	3.2
CN^- (C)	−67.8 ± 2.4[c]	0.7	2.5	2.1	1.0	−0.4	−0.3
CN^- (N)[b]		2.3	3.1	2.5	2.5	0.8	0.9
SH^-	−71.1 ± 4.2	11.0	12.2	12.3	9.5	7.9	7.8
Cl^-	−73.2 ± 1.3	11.7	11.8	11.4	8.8	6.7	6.6
$HCOO^-$ (syn)	−73.6 ± 4.2	5.7	7.5	7.2	4.7	2.6	2.6
$HCOO^-$ (anti)[b]		7.6	8.6	8.1	7.7	5.7	5.6
MeO^-	−121.9 ± 1.9[c]	8.9	12.5	12.9	11.1	7.9	7.1
F^-	−127.6 ± 2.9	−1.6	−0.7	0.5	4.6	2.9	2.3
	MAD=	6.5	8.3	8.1	4.1	2.8	2.6

[a] Geometries have been optimized with the B3LYP/6-31+G(d,p) method. The enthalpies quoted at other levels of theory were single-point calculations at the B3LYP/6-31+G(d,p) optimized geometry. [b] Not taken into account in MAD calculations. [c] Uncertainty of the mean at the 95% confidence level.

these complexes are given in Table 1. Indeed, methanol provided more comprehensive gas-phase experimental hydrogen-bond enthalpies than either H_2O or HF, the HBDs most extensively studied by theoreticians. The thirteen HBAs considered correspond to diverse acceptor sites (C, N, O, F, S, Cl, and Br), functionalization (e.g., oxygen bases correspond to CH_3OH, CH_3O^- and $HCOO^-$), and substitution (e.g., the nitrogen atom of amines bears an increasing number of methyl and ethyl groups). This chemical diversity of HBAs leads to a wide scale of enthalpies, from −17 to −128 kJ mol^{-1} for the methanol homodimer and the MeOH···F^- heterodimer, respectively. As such, they provide a basis for critical comparison with theory and allow generalizations to be made that will be applicable in larger, more complex, hydrogen-bonded complexes.

The article is organized as follows. We first present critically the experimental data. A computational section lists the basis sets (6-31+G(d,p), 6-311+G(3df,2p), and aug-cc-pVTZ), the level of theory (B3LYP density functional theory and full and frozen core (fc) MP2 ab initio level), and the computational strategy that have been chosen. The geometric characteristics of the complexes are then analyzed. We focus our attention on the basis set superposition error (BSSE), which may represent a large part of the electronic interaction energy. Next, we compare the various levels of theory with experiment by means of the mean absolute deviation (MAD) between calculated and experimental enthalpies and of linear regressions. Finally, to explain the deficiency of the B3LYP method to reproduce the effect of alkylation on the nitrogen HB basicity of amines, the intermolecular perturbation theory (IMPT)[30] is applied to two complexes of methanol with amines.

II. Experimental Data

The experimental enthalpies of methanol hydrogen-bonded complexes at 298 K are collected in Table 1 and commented on below. They were all obtained by determining the equilibrium constants of the reaction MeOH + B = MeOH···B at various temperatures and treating these data with Van't Hoff plots.

MeOH. The self-association in methanol vapor has been investigated by several researchers with varied results.[29] We have selected the NMR spectroscopic result,[31] because data were obtained over a large temperature range (333−468 K) and fitted with a simple monomer−dimer model.

$MeNH_2$, Me_2NH, Me_3N, and Et_3N. We have retained the values derived from pressure, volume, and temperature measurements.[32] Because they were obtained in the same work by the same method, the results of this systematic study[32] of the methanol−amine complexes are expected to be self-consistent. Moreover, the methanol−trimethylamine value is supported by an infrared result.[33]

Et_2NH. A single value (from vapor density measurements) is available,[34] which seems chemically consistent with the above results,[32] being higher than the Me_2NH value and lower than the Et_3N value.

F^-, Cl^-, and Br^-. The numerous existing data on the methanol−halide complexes have been evaluated.[35] We have retained the values (obtained from pulsed ionization high-pressure mass spectrometry (PHPMS)) recommended in this evaluation.[35] PHPMS techniques use relatively large pressures and thus enable a much better control of temperature than other mass spectrometric methods.

CN^- and MeO^-. We have worked out the average of PHPMS values found in the NIST database.[36] One seemingly deviant value[37] has been excluded in the case of MeO^-.

SH^- and $HCOO^-$. The complexes of methanol with both anions have a single PHPMS value.[38,39]

The experimental uncertainties are those given by the authors (no uncertainty is given for Et_2NH), except for CN^- and MeO^- where they correspond to the uncertainty of the mean at the 95% confidence level.

III. Calculations

All enthalpy calculations were carried out using the *Gaussian 98*[40] suite of programs. The geometries of the monomers and dimers were fully optimized at the B3LYP[41,42] level using the 6-31+G(d,p) basis set.[43−45] This split valence 6-31G basis, augmented with polarization functions[46] on all atoms and diffuse functions[47] on non-hydrogen atoms, appears to be the minimum basis set required to describe the structure and the vibrational spectra of hydrogen-bonded complexes at the B3LYP level.[48,49] The largest complex studied, $CH_3OH···N(CH_2CH_3)_3$, is defined by 266 contracted atomic orbital basis functions with this basis set. All stationary points were confirmed as true minima via vibrational frequency calculations.

The binding enthalpy, ΔH°_{298}, of a hydrogen-bonded complex is the enthalpy of reaction 2 at 298.15 K and 1 bar. It is given by eq 3. The term ΔE_{el} is the electronic interaction energy,

$$\mathrm{MeOH} + \mathrm{B} \rightleftarrows \mathrm{MeOH}\cdots\mathrm{B} \tag{2}$$

$$\Delta H^{\circ}_{298} = \Delta E_{\mathrm{el}} + \mathrm{BSSE} + \Delta\mathrm{ZPVE} + \Delta E_{\mathrm{vib,therm}} + \Delta E_{\mathrm{rot}} + \Delta E_{\mathrm{trans}} + \Delta nRT \tag{3}$$

evaluated at a particular level of theory (vide infra). The BSSE term corresponds to the spurious stabilization of the complex introduced by the computation of ΔE_{el} by the supermolecular approach. We have calculated this term by means of the full counterpoise method[50] with fragment relaxation.[51] The third term is the zero-point vibrational energy contribution to the binding enthalpy. The remaining vibrational term, $\Delta E_{\mathrm{vib,therm}}$, is the change in the vibrational energies in going from 0 to 298 K. They were computed at the B3LYP/6-31+G(d,p) level within the harmonic approximation with a scaling factor of 0.9804.[52] The last terms that contribute to ΔH are thermal terms, which account for the loss of rotational and translational degrees of freedom, and the change in the number of moles of gas ($\Delta n = -1$), respectively. They were evaluated classically: $\Delta E_{\mathrm{trans}} = -{}^{3}/_{2}RT$; $\Delta E_{\mathrm{rot}} = -{}^{3}/_{2}RT$ if B = a polyatomic nonlinear molecule, $-RT$ if B = a linear molecule, and 0 if B is an atomic species.

Because ΔE_{el} is the dominant term in the enthalpy expression, it is imperative to compute this energy at a sufficiently high level of theory and with extended basis sets. So, single-point energy (ΔE_{el} and BSSE) calculations were performed at the B3LYP and full and/or frozen core[53] (fc) MP2[53,54] levels using the larger basis sets 6-311+G(3df,2p)[55−58] (Pople style) and aug-cc-pVTZ[59−62] (Dunning style). The first basis set is the largest one used in the G2 technique;[53] the B3LYP/6-311+G(3df,2p) approach compares well with the G2(MP2) theory for the methanol−water dimer.[63] The $\mathrm{CH_3OH}\cdots\mathrm{N(CH_2CH_3)_3}$ complex is defined by 522 and 851 contracted atomic orbital basis functions with the 6-311+G(3df,2p) and aug-cc-pVTZ basis sets, respectively.

IMPT calculations were used to perform the decomposition of the electronic interaction energy for the complexes of methanol with methylamine, the least alkylated amine, and triethylamine, the most alkylated one, to understand the effect of alkylation on the various components of ΔE_{el}. The method of Hayes and Stone[30] was used, as implemented in version 6.5 of the program CADPAC,[64] with the 6-31G(d) basis set. IMPT/6-31G(d)//B3LYP/6-31+G(d,p) calculations yield ΔE_{el} as the sum of five components (eq 4), namely, electrostatic (classical

$$\Delta E_{\mathrm{el}} = E_{\mathrm{es}} + E_{\mathrm{er}} + E_{\mathrm{pol}} + E_{\mathrm{ct}} + E_{\mathrm{disp}} \tag{4}$$

Coulombic) energy (E_{es}), exchange repulsion (E_{er}), polarization (E_{pol}), charge transfer (E_{ct}), and dispersion energy (E_{disp}). The first two terms are first-order, the others second-order. An important feature of the IMPT method is that E_{ct} and E_{pol} are free of BSSE, although the division between these terms is not completely independent of basis set.[65]

IV. Results and Discussion

IV.A. Geometries of Methanol−Base Complexes. The distances and angles d, D, r, θ, and ϕ that most simply define the HB geometry are defined in Figure 1 and summarized in Table 2. A linear hydrogen bond is preferred, since the average of θ angles, equal to 173.2 ± 1.7° (95% confidence level), approaches 180°. Individual geometries are commented on below with a focus on the directionality, ϕ.

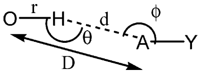

Figure 1. Angular and radial parameters describing the HB geometry.

TABLE 2: Selected Geometric Parameters of the Hydrogen-Bonded Complexes of Methanol with a Variety of Acceptors from B3LYP/6-31+G(d,p) Optimized Structures: HB Length, *d* (Å), Distance between Heavy Atoms, *D* (Å), OH Bond Lengthening, Δ*r* (Å)[c], Linearity, *θ* (°), and Directionality, *ϕ* (°), as Shown in Figure 1

acceptor	d	D	Δr	θ	ϕ
MeOH	1.896	2.867	0.0088	174.9	114.4 (H···OC)
$\mathrm{MeNH_2}$	1.900	2.878	0.0182	172.5	109.7[a]
$\mathrm{Me_2NH}$	1.889	2.868	0.0198	172.3	108.4[a]
$\mathrm{Et_2NH}$	1.890	2.870	0.0206	172.1	108.5[a]
$\mathrm{Me_3N}$	1.892	2.871	0.0199	171.9	107.5[b]
$\mathrm{Et_3N}$	1.944	2.919	0.0191	169.9	108.4[b]
$\mathrm{Br^-}$	2.330	3.305	0.0237	168.6	
$\mathrm{SH^-}$	2.211	3.206	0.0356	171.8	97.1 (H···SH)
$\mathrm{Cl^-}$	2.133	3.117	0.0290	170.0	
$\mathrm{CN^-}$ (C)	1.844	2.850	0.0446	173.8	179.7 (H···CN)
$\mathrm{CN^-}$ (N)	1.736	2.734	0.0375	173.2	177.6 (H···NC)
$\mathrm{HCO_2^-}$ (syn)	1.699	2.698	0.0344	178.5	121.2 (H···OC)
$\mathrm{HCO_2^-}$ (anti)	1.625	2.631	0.0452	173.8	120.5 (H···OC)
$\mathrm{MeO^-}$	1.262	2.426	0.1992	178.2	109.9 (H···OC)
$\mathrm{F^-}$	1.341	2.417	0.1126	176.9	

[a] Average of (H···NH) and (H···NC) angles. [b] Average of (H···NC) angles. [c] $\Delta r = d(\mathrm{O-H})$ in the complex $- d(\mathrm{O-H})$ of the methanol molecule ($d(\mathrm{O-H}) = 0.964\,94$ Å).

MeOH. As expected, the hydrogen bond (i.e. the O···H vector) points to a putative sp^3 oxygen lone pair in a quasi-tetrahedral arrangement ($\phi = 114°$) around the acceptor oxygen.

Amines. The hydrogen bond points to the putative sp^3 nitrogen lone pair. For the $\mathrm{MeOH}\cdots\mathrm{NMe_3}$ complex, microwave spectroscopy yields $d = 1.92(5)$ Å and a dipole moment of 2.87 ± 0.15 D[66] in fair agreement with our B3LYP/6-31+G(d,p) computed values of 1.89 Å and 2.95 D.

SH$^-$. The hydrogen bond is nearly perpendicular to the S−H bond ($\phi = 97°$). This arrangement around sulfur is common in sulfides.[23,67]

CN$^-$. There are two potential HBA sites: the carbon and the nitrogen atoms. At the B3LYP/6-31+G(d,p) level, the C complex is preferred by 0.8, 1.6, and 2.2 kJ/mol on the ΔE_{el}, ΔH, and ΔG energy scales, respectively. Moreover, enthalpies computed at the same geometry with extended basis sets (6-311+G(3df,2p) and aug-cc-pVTZ) and at the MP2 level are always lower for the C complex by 0.5−1.3 kJ/mol^{-1}. However, these enthalpy differences fall within the experimental uncertainty, which amounts to at least 3.3 kJ mol^{-1}.[68] These results suggest a mixture of C and N complexes in the methanol−cyanide vapor. The same conclusion has been reached for the water−cyanide complex.[69,70] As far as the directionality is concerned, the hydrogen bond points to a putative sp lone pair of the carbon (nitrogen) atom (ϕ = 180° and 178° for the C and N complexes, respectively).

HCOO$^-$. The geometry of the methanol−formate complex has been optimized from four starting geometries. Conformations syn, anti, and linear correspond to a two-centered[3] hydrogen bond, while a three-centered[3] hydrogen bond can also be formed if the hydrogen bond points to the middle of the oxygen−oxygen distance. We have not found any stable two-centered linear or three-centered complex. The anti complex is

TABLE 3: Electronic and Vibrational Contributions to the Binding Enthalpy (eq 3) (in kJ mol^{-1}) at Various Levels of Theory,[a] for the Hydrogen-Bonded Complexes of Methanol with Various Acceptors

	B3LYP/6-31+G(d,p)				B3LYP/ 6-311+G(3df,2p)		B3LYP/ aug-cc-pVTZ		MP2(full)/ 6-311+G(3df,2p)		MP2(full)/ aug-cc-pVTZ		MP2(fc)/ aug-cc-pVTZ	
acceptors	$-\Delta E_{el}$	BSSE	ΔZPVE	$\Delta E_{vib,therm}$	$-\Delta E_{el}$	BSSE	$-\Delta E_{el}$	BSSE	$-\Delta E_{el}$	BSSE	$-\Delta E_{el}$	BSSE	$-\Delta E_{el}$	BSSE
MeOH	24.67	3.19	5.68	11.04	20.62	1.25	19.75	0.35	25.88	3.78	27.78	5.01	25.41	2.64
$MeNH_2$	32.69	3.70	6.58	10.38	27.34	1.04	26.87	0.40	33.47	3.98	36.68	6.09	33.67	3.00
Me_2NH	31.92	3.34	6.41	10.67	27.24	1.24	26.64	0.53	36.06	4.62	40.41	7.87	36.42	3.70
Et_2NH	31.75	3.44	6.37	10.72	27.47	1.45	26.70	0.61	40.42	5.60	45.88	9.72	40.95	4.60
Me_3N	30.34	3.27	5.77	8.59	26.01	1.42	25.28	0.60	38.30	5.77	43.60	9.98	38.27	4.38
Et_3N	26.71	3.38	6.11	10.81	22.84	1.80	22.84	0.90	42.82	7.07	50.68	13.39	43.94	6.09
Br^-	60.51	7.63	1.88	4.86	52.73	0.64	52.78	0.36	60.73	4.60	73.79	15.87	66.08	8.04
SH^-	63.78	1.14	3.17	8.08	63.07	1.61	61.80	0.43	69.60	5.46	74.40	8.68	69.96	4.09
Cl^-	62.53	0.77	1.94	4.57	63.49	1.77	62.38	0.31	70.34	5.67	74.86	8.01	70.71	3.79
CN^-(C)	71.97	2.19	3.40	7.99	69.09	1.12	69.00	0.56	74.14	4.59	78.44	7.48	74.18	3.35
CN^-(N)	71.15	2.44	3.78	8.16	69.22	1.23	69.32	0.75	73.70	5.12	80.62	10.38	73.95	3.81
HCO_2^- (syn)	76.13	2.71	5.40	10.01	73.39	1.81	72.48	0.61	80.07	5.65	83.85	7.39	80.54	4.11
HCO_2^- (anti)	73.13	2.24	4.28	10.49	71.55	1.67	70.94	0.58	76.44	5.69	80.05	7.31	76.88	4.03
MeO^-	116.69	5.90	−2.39	10.11	111.58	4.34	108.15	1.36	119.60	10.97	122.74	10.96	119.65	7.08
F^-	127.95	3.88	−2.28	3.39	129.18	5.96	123.09	1.11	128.25	10.32	129.02	9.40	125.61	5.38

[a] Geometries have been optimized with the B3LYP/6-31+G(d,p) method. The energies and basis set superposition errors quoted at other levels of theory were single point calculations at the B3LYP/6-31+G(d,p) optimized geometry.

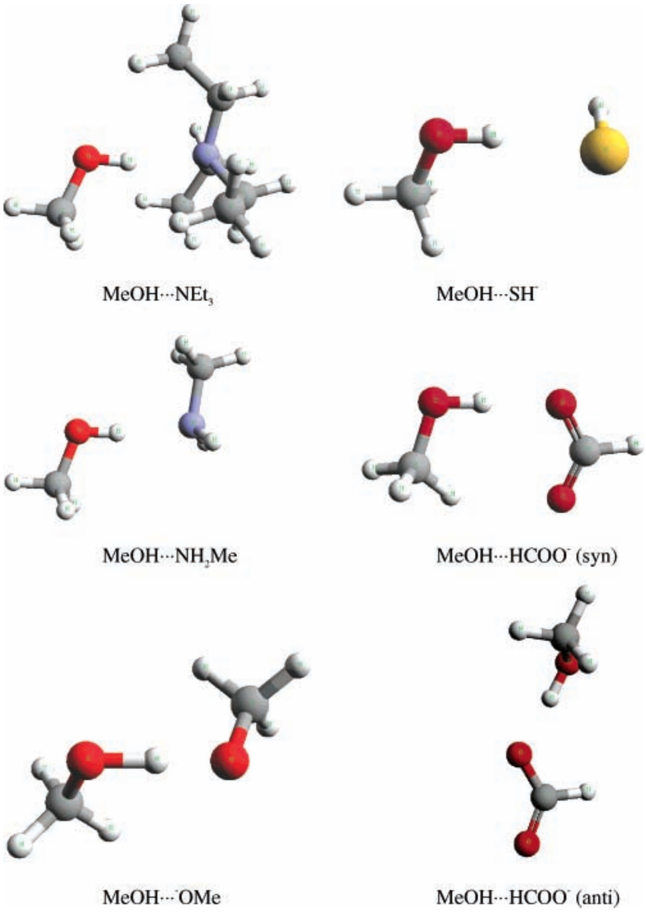

Figure 2. Optimized structures (B3LYP/6-31+G(d,p)) of representative complexes.

3 kJ mol^{-1} higher in energy than the syn one. The higher stability of the syn complex compared to the anti one can possibly be explained by a secondary C−H···O hydrogen bond (see Figure 2) whose characteristics are as follows: $d = 2.556$ Å, $\theta = 142.7°$, and ϕ(H···OC) = 104.3°. Note that the syn geometry is also slightly preferred by hydrogen-bonded carboxylate anions in the solid state.[71] In the syn conformation, the hydrogen bond lies along the putative position of an sp^2 lone pair on oxygen ($\phi = 121°$).

CH_3O^-. The B3LYP/6-31+G(d,p) potential energy surface shows one minimum along the coordinate defined by the COOC dihedral angle, corresponding to COOC = 90°. The structure is asymmetrical, and the O−H···O arrangement is described by two different OH bond lengths, d(O−H) = 1.164 Å and d(O···H) = 1.262 Å. Nevertheless, it shows the shortest HB length and the greatest OH bond lengthening of the series. This result is qualitatively confirmed by an MP2/6-311+G(d,p) study.[72]

The optimized structures of representative complexes determined in this study are displayed in Figure 2.

IV.B. Basis Set Superposition Error. The BSSE-uncorrected electronic interaction energy, ΔE_{el}, and the BSSE, calculated with three different basis sets (Pople, extended Pople, extended Dunning) and three levels of theory (B3LYP, fc MP2, full MP2) are presented in Table 3. The importance of BSSE in the various calculations is evaluated as the percentage %BSSE = 100BSSE/ΔE_{el}. It can be as low as 0.5% for MeOH···Cl$^-$ at B3LYP/6-311+G(3df,2p) and as high as 26% for MeOH···NEt$_3$ at full MP2/aug-cc-pVTZ.

At the B3LYP level, the %BSSE decreases almost systematically with the increasing size of the basis set, i.e., in the order 6-31+G(d,p) > 6-311+G(3df,2p) > aug-cc-pVTZ, as expected. However, at the full MP2 level, the aug-cc-pVTZ BSSE is always larger than the 6-311+G(3df,2p) one, except for the two strongest complexes, for which the two corrections are similar.

As far as the level of theory is concerned, the BSSE correction is much larger at the full MP2 correlated level than at the density functional level, for the same basis set. However, the fc MP2 BSSE is always about half of the full MP2 BSSE.

Since the electronic interaction energies computed at the full MP2 level are always lower than those calculated at the fc MP2 level, it is interesting to compare (ΔE_{el} + BSSE) for the full and frozen core calculations, to know if the much larger calculation time for full MP2 yields a true improvement in the BSSE-corrected electronic interaction energy. In fact, full MP2(ΔE_{el} + BSSE) never differs by more than 1 kJ mol^{-1} from fc MP2(ΔE_{el} + BSSE). Thus, the frozen core approach is satisfactory to reproduce HB enthalpies with sufficient accuracy. One might judge the calculations that do not freeze core electrons to be more rigorous, but unless the basis set includes extra core functions, there is some imbalance in the treatment of core−core versus core−valence correlation. In other words, correlating the core electrons requires basis functions able to carry out this purpose. In this regard, 6-311+G(3df,2p) and aug-cc-pVTZ basis sets might be ill-suited.[73]

IV.C. Comparison between Experimental and Calculated Binding Enthalpies. The comparison is made by means of the deviation of theoretical enthalpies from experiment, $\delta(\Delta H)$, and the mean absolute deviation, MAD, defined by eqs 5 and 6, respectively (n is the number of HBAs), and reported in Table 1.

$$\delta(\Delta H) = \Delta H(\text{theor.}) - \Delta H(\text{exp.}) \qquad (5)$$

$$\text{MAD} = [\sum_{i}^{n} |\Delta H(\text{theor.})_i - \Delta H(\text{exp.})_i|]/n \qquad (6)$$

It is found, by considering individual deviations or, more briefly, MADs, that the deviations

(1) do not decrease, at the B3LYP level, by increasing the size of the basis set.

(2) are always smaller for MP2 than for B3LYP calculations, for the same basis set.

(3) are smaller, at the MP2 levels, for the aug-cc-pVTZ than for the 6-311+G(3df,2p) basis sets.

(4) do not decrease when full instead of frozen core MP2 calculations are performed.

Thus, the agreement with experiments follows the order

$$\text{fc MP2/aug-cc-pVTZ} \approx \text{full MP2/aug-cc-pVTZ} > \text{full MP2/6-311+G(3df,2p)} > \text{B3LYP/6-31+G(d,p)} > \text{B3LYP/6-311+G(3df,2p)} \approx \text{B3LYP/aug-cc-pVTZ}.$$

It seems rather trivial to conclude that the absolute binding enthalpy of methanol complexes is best reproduced by MP2 calculations, an explicitly correlated level of theory, with the aug-cc-pVTZ basis set, a correlation-consistent basis set, or, in other words, that MP2 is a better correlated model than B3LYP. It is more interesting to remark that, while deviations are generally positive (i.e., calculations underestimate the HBA strength), a few become negative at the higher MP2/aug-cc-pVTZ level. This probably means that calculations begin to converge to the exact energy (insofar as the experimental enthalpies are free of errors). This assertion is supported in the case of the methanol dimer by the agreement between our computed counterpoise corrected binding energy MP2 (fc and full)/aug-cc-pVTZ value of -22.77 kJ mol^{-1} and the value of -22.80 kJ mol^{-1} expected to be the basis set limit at the CCSD(T) level.[74] This strong agreement between MP2/aug-cc-pVTZ and experimental enthalpies is also shown by comparing $\delta(\Delta H)$ and the experimental uncertainty. $\delta(\Delta H)$ falls inside the experimental error, except for the acceptors with second- and third-row sites (Cl^-, SH^-, and Br^-) and for MeO^-. Therefore, it appears that the geometry optimization at the rather low B3LYP/6-31+G(d,p) level (a choice made in order to study large biological complexes in future work) was not detrimental to the accuracy of binding enthalpies, as long as the electronic interaction energy and BSSE are calculated at a correlated level with a large correlated-consistent basis set.

Chemists may be satisfied by a *relative* agreement of theory with experiment. In our case, it may be sufficient that theory reproduces the order of HBA strength. To study this relative agreement, we have performed the regression of ΔH(theor.) on ΔH (exp.) according to eq 7 by the least-squares method

$$\Delta H(\text{theor.}) = a\Delta H(\text{exp.}) + b \qquad (7)$$

(assuming experimental enthalpies free of errors) for the enthalpies calculated using the six theoretical methods given in Table 1. The results are presented in Table 4. They confirm that the MP2 method performs better than the B3LYP one ($r^2 = 0.994-0.995$ instead of $0.984-0.985$, and a standard error for MP2 of ca. half that for B3LYP). Nevertheless, B3LYP yields good statistics, which indicate that B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations of the binding enthalpies of methanol complexes yield a satisfactory order of HBA strength from methanol to F^-. The determination coefficients obtained in this study are greater than those found previously,[23,24] at similar levels, in the relative comparison between an experimental descriptor of HBA strength and calculated energies of H_2O complexes ($n = 15$, $r^2 = 0.90$)[23] or HF complexes ($n = 40$, $r^2 = 0.883-0.928$ according to the type of energy calculated).[24]

TABLE 4: Statistics for the Regression of ΔH(theor.) on ΔH(exp.) for the Six Theoretical Levels[a]

theoretical level	r^2	a	b^b	s^b
B3LYP/6-31+G(d,p)	0.984	1.01 (0.04)	7 (3)	5.0
B3LYP/6-311+G (3df, 2p)//B3LYP/6-31+G(d,p)	0.984	1.02 (0.04)	9 (3)	5.0
B3LYP/aug-cc-pVTZ//B3LYP/6-31+G(d,p)	0.985	1.01 (0.04)	9 (3)	4.7
MP2 (full)/6-311+G(3df,2p)//B3LYP/6-31+G(d,p)	0.994	0.93 (0.02)	0 (2)	2.7
MP2 (full)/aug-cc-pVTZ//B3LYP/6-31+G(d,p)	0.995	0.94 (0.02)	−1 (2)	2.5
MP2 (fc)/aug-cc-pVTZ//B3LYP/6-31+G(d,p)	0.995	0.95 (0.02)	−1 (2)	2.5

[a] r^2 is the determination coefficient and s the standard error of the fit. The slope a and the intercept b are followed by their standard error in brackets. Only the most stable complexes are taken into account in the regression (i.e., CN^-(C) and HCO_2^- (syn)). [b] kJ mol^{-1}.

The main reason for the deterioration in the determination coefficients in Table 4 in going from the MP2 to the B3LYP data sets comes from the behavior of amines. The experimental order of the binding enthalpy of amines

$$Et_3N > Me_3N \approx Et_2NH > Me_2NH > MeNH_2$$

indicates that increasing the number and length of alkyl groups on the nitrogen atom makes the amine a better HBA. This order is well-reproduced by MP2 calculations but is lost in B3LYP ones. This is illustrated in Figure 3, which shows a part of the B3LYP and MP2 regression lines of eq 7 in the region of amines. The inability of the B3LYP method to reproduce the effect of alkyl substituents on the HBA strength of amines is studied in the next section.

IV.D. Quantum Chemistry Study of the Effect of Alkyl Substituents on the Amine Hydrogen-Bond Basicity. As is apparent in Table 1 and Figure 3, the B3LYP method appears to underestimate the stability of methanol−amine complexes, with this underestimation becoming more pronounced as the degree of alkylation of the amine increases. For example, at B3LYP/aug-cc-p-VTZ, the differences, in kilojoules per mole, between the calculated and experimental hydrogen-bond enthalpies are as follows:

$$MeNH_2\ (4.0) < Me_2NH\ (6.9) < Me_3N\ (8.7) \approx Et_2NH\ (9.1) < Et_3N\ (16.5)$$

In contrast, the differences between MP2 theory (with the same basis set as B3LYP) and experimental results oscillate around zero and show no relation to the number and length of

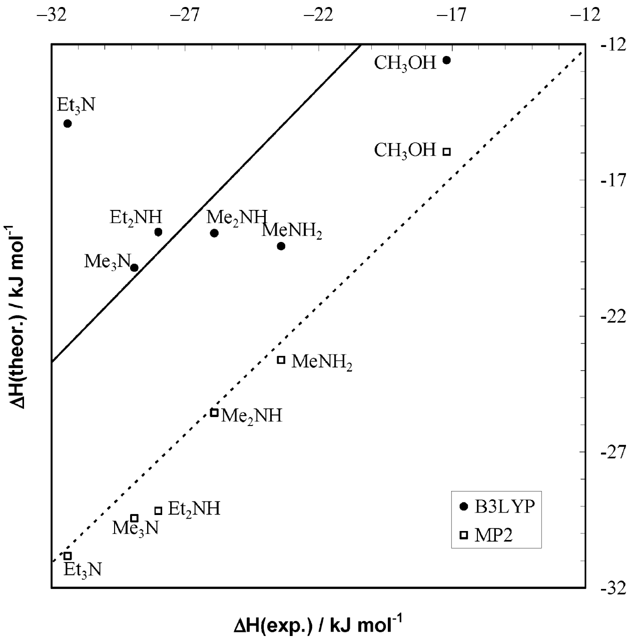

Figure 3. Plot of ΔH(theor.) against ΔH(exp.) for the B3LYP/aug-cc-pVTZ//B3LYP/6-31+G(d,p) (●) and MP2(fc)/aug-cc-pVTZ//B3LYP/6-31+G(d,p) (□) data sets showing the position of amines with respect to the least-squares lines.

TABLE 5: Electronic Interaction Energy Components of MeOH···NEt$_3$ and MeOH···NMeH$_2$ Complexes Calculated at the IMPT/6-31G(d)//B3LYP/6-31+G(d,p) Level (kJ mol^{-1})[a]

	E_{es}	E_{er}	E_{pol}	E_{ct}	E_{disp}	ΔE_{el}	%(E_{disp}/ ΔE_{el})	%($\lvert E_{disp}\rvert$/ $\Sigma\lvert E_i\rvert$)[b]
MeNH$_2$	−59.0	50.6	−5.9	−7.4	−8.7	−30.2	29	7
Et$_3$N	−53.6	54.5	−6.4	−7.6	−19.6	−32.7	60	14

[a] E_{es} = electrostatic interaction, E_{er} = exchange repulsion, E_{pol} = polarization, E_{ct} = charge transfer, E_{disp} = dispersion and ΔE_{el} = total electronic interaction energy. [b] Ratio of absolute dispersion energy value to the sum of the absolute values of the five energy components.

alkyl groups. This very noticeable deficiency of the B3LYP method and the success of the MP2 one raise the question about the nature of the alkyl substituent effect on the hydrogen bond. In organic chemistry, the alkyl substituent effect on reactivity has been the subject of much debate, and various mechanisms (inductive, hyperconjugative, polarizability, steric) have been suggested.[75−85] In the field of gas-phase proton basicity, related to the gas-phase hydrogen-bond basicity[86] studied here, the increase in the proton affinity of amines upon alkylation has been attributed[87] to a polarizability effect, i.e., a charge-induced dipole interaction between the charged nitrogen and the alkyl groups. Indeed, the decomposition of the electronic protonation energies of alkylamines into electrostatic, charge transfer, and polarization terms[88] confirms the significant increase of E_{pol} with alkylation.[89]

We also decided to perform a decomposition of the electronic HB interaction energy, by means of the IMPT[30] method. We chose two amines: the least and most alkylated ones, NH$_2$Me and NEt$_3$ respectively. The results of IMPT/6-31G(d)//B3LYP/6-31+G(d,p) calculations are presented in Table 5 for their complexes with MeOH. They show that the widest variation in the energy components, in going from one methyl to three ethyls, arises from the dispersion term. The ratios $E_{disp}/\Delta E_{el}$ as well as $|E_{disp}|/(|E_{es}| + |E_{er}| + |E_{pol}| + |E_{ct}| + |E_{disp}|)$ increase by a factor of 2 from MeNH$_2$ to NEt$_3$.

Two conclusions can be drawn. First, the differences between B3LYP and experimental HB binding enthalpies arise from the B3LYP inability to satisfactorily take into account electron correlation and, therefore, dispersion, which has its origin in molecular polarization and electron correlation. This deficiency of B3LYP, and many other density functionals, is well-known for van der Waals complexes and weak hydrogen bonds in which the dispersion contribution is important.[90−93] This study shows that B3LYP is also deficient for rather strong hydrogen bonds (remembering that amines are the strongest HBA of organic neutral molecules[5,11,12]) insofar as the HBA site is significantly alkylated. So, we fear that B3LYP might not adequately describe the HBA strength not only of secondary and tertiary amines but also of highly alkylated ethers, sulfides, and phosphines. Second, the enhancing basicity effect of alkyl groups does not have the same origin according to whether one considers proton (Brönsted) basicity or hydrogen-bond basicity. In the protonated bases, alkyls mainly modify the polarization energy component, while in neutral hydrogen-bonded complexes, they mostly affect the dispersion energy component.

V. Conclusion

We have calculated the enthalpy of hydrogen bonding of methanol with thirteen neutral and anionic hydrogen-bond acceptors at various levels of theory and with several basis sets. B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations are generally able to give the correct order of hydrogen-bonding basicity, except for alkylamines for which they fail dramatically. Only MP2(fc and full)/aug-cc-pVTZ//B3LYP/6-31+G(d,p) calculations are capable of reproducing the experimental enthalpies within the experimental error, for first-row acceptor atoms (N, O, F), and the hydrogen-bond basicity of variously alkylated amines, from MeNH$_2$ to NEt$_3$. Thus, the choice of the frozen core method must be favored because of the CPU time saved compared with the full MP2 method. IMPT calculations on the complexes of these amines show that the dispersion energy contribution to the electronic interaction energy increases dramatically with the degree of alkylation. It can be concluded that studies of the hydrogen bond to highly alkylated atomic sites (Alk$_2$NH, Alk$_2$O, Alk$_2$S, Alk$_3$N, and Alk$_3$P) might require the use of a method that accounts for dispersion effects, such as the MP2 method with correlation-consistent basis sets.

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