

The Hydrogen-bond Basicity of Carbenes

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Abstract: We have evaluated theoretically in the gas-phase (MP2/aug-cc-pVTZ) the hydrogen-bond basicity of simple carbenes and vinylidenes and compared them to the corresponding nitrogen and oxygen derivatives using HF as Lewis acid. These values fit conveniently with B values only if sp^3 and sp^2 atoms are treated separately, which is a consequence of the gas-phase (calculated) vs. solution (measured) effects.

Keywords: carbenes, N-heterocyclic carbenes, Gas-phase MP2 calculations, hydrogen-bond basicity (HBB), β scale of HBB.

INTRODUCTION

SINGLET carbenes, being Lewis-bases (LBs), form hydrogen bonds (HBs) with Lewis acids (LAs).^[1] These HBs were first studied theoretically by Pople *et al.* (LA = HF).^[2,3] We started our interest in these systems in 1996,^[4] and continued in 2017.^[5] Several other papers were published on carbenes HBs by Standard,^[6,7] Howard,^[8] Hollóczki^[9] and Sander.^[10] However, the only data of the hydrogen bond basicity, HBB, of singlet carbenes in a scale of HBB is the prediction by Platts based on single point B3LYP/6-311G(d,p) calculations concerning the B value of Arduengo's carbene (1,3,4,5-tetramethyl-imidazolide) to be 0.83.^[11] In the Abraham scale, a value of 0.83 corresponds to a very basic substance (triethylamine, $B = 0.79$).^[12,13]

The domains where the HBB of carbenes are relevant is very large;^[14–19] as a particular interesting example we note that it has been reported that a stable carbene is present at the active site of a thiamin enzyme where weak interactions, like HBs, play a major role.^[20]

COMPUTATIONAL DETAILS

All electronic structure calculations were performed with the Gaussian 09 program package.^[21] The geometries of monomers and complexes were optimized without any restriction using the second-order Møller-Plesset

perturbation theory (MP2)^[22] with the aug-cc-pVTZ basis set.^[23,24] All stationary points were confirmed as minimum energy by the absence of imaginary frequencies. E_b , the binding energy, is defined as the difference between the total energy of the complex and the sum of that of the isolated monomers in their minima configuration. The minima of the electrostatic potential (MEP) were analyzed with the DAMQT 2.1.0. program.^[25]

RESULTS AND DISCUSSION

The aim of the present paper is to explore theoretically the HBB of carbenes by calculating the gas-phase binding energies with HF of a series of oxygen, nitrogen and carbon derivatives, all of them having lone pairs (LPs) some of them (oxygen and nitrogen derivatives) having known values of B . We have considered sp^3 carbenes (RR'C:) and sp^2 vinylidenes (RR'C=C:). All the studied carbenes except methylene (:CH₂) have the singlets more stable than the triplets.^[26] The same happens with the vinylidenes (this work) where the singlet/triplet gaps are -218.6 kJ·mol⁻¹ (:CCH₂) and -80.3 kJ·mol⁻¹ (:CCF₂).

In a first attempt we selected the compounds represented in Scheme 1.

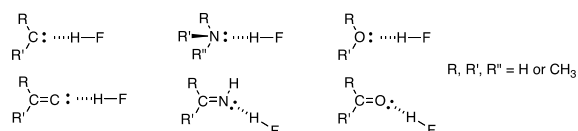
But, during the optimization process of both carbenes and vinylidenes, if R, R', R'' is CH₃, then a 1,2-hydrogen shift^[27] occurs and the optimized structure is an olefin. In two vinylidenes, (CH₃)₂C=C: and (NH₂)₂C=C:, the

Table 1. Calculated (gas-phase) and experimental (solution) measures of HBB: β_2^H , and B values are all from Abraham^[12,13,18] except one value (imidazolidene) from Platts.^[11]

Bases	E_b / kJ·mol ⁻¹	Abraham B	Predicted B	Abraham β_2^H (b)	MEP-min / kJ·mol ⁻¹
sp³					
NH ₃ (ammonia)	-54.1	0.56		0.60	
CH ₃ NH ₂ (methylamine)	-60.1	0.58		0.70	
(CH ₃) ₂ NH (dimethylamine)	-63.0	0.66		0.72	
H ₂ O (water)	-37.5	0.46		0.38	
CH ₃ OH (methanol)	-42.9	0.47		0.41	
(CH ₃) ₂ O (dimethyl ether)	-45.6	0.41		0.43	
:CH ₂ (methylene)	-49.3		0.51		-241.5
:C(CH ₃) ₂	-68.1		0.68		-306.4
:CH(OCH ₃)	-64.4		0.65		-280.9
:CH(NH ₂)	-71.3		0.71		-328.2
:C(NH ₂) ₂	-73.0		0.72		-330.8
Arduengo's carbene (imidazolidene)	-83.6	0.83 ^(a)			-359.7
sp²					
H ₂ C=NH	-52.0		0.63		
CH(CH ₃)=NH	-61.0		0.81		
(CH ₃) ₂ C=NH	-57.1		0.73		
CH(CH ₃ O)=NH (methyl formimide)	-55.4		0.70		
CH(NH ₂)=NH (formamidine)	-77.6		1.14		
C(NH ₂) ₂ =NH (guanidine)	-71.3	1.04			
F ₂ C=NH	-37.1		0.34		
H ₂ C=O (formaldehyde)	-35.8	0.33			
CH(CH ₃)=O (acetaldehyde)	-41.7	0.45		0.38	
(CH ₃) ₂ C=O (acetone)	-45.8	0.49		0.49	
CH(CH ₃ O)=O (methyl formate)	-39.0	0.38		0.39	
CH(NH ₂)=O (formamide)	-56.1	0.60		0.61	
C(NH ₂) ₂ =O (urea)	-59.3	0.84			
F ₂ C=O	-20.1		0.00		
H ₂ C=C: (vinylidene)	-37.7		0.35		-189.0
F ₂ C=C: (difluorovinylidene)	-28.3		0.16		-128.6

^(a) Platts value.^[11]

^(b) β_2^H values fit slightly better but there are less compounds.



Scheme 1.

optimization leads to structures where the terminal carbon approaches the substituent (CH₃ or NH₂). Thus, we calculated another series of compounds (Figure 1 and Table 1).

We have reported the values in Table 1. We give two different scales of HBB. The β_2^H scale of Abraham *et al.*^[18] denotes the solute HBB towards a single hydrogen bond acid and the B -scale of Abraham *et al.*^[11,12] denotes the solute HBB when surrounded by hydrogen bond acids.

We have represented the B values against the E_b ones and it is apparent that the sp³ and sp² atoms belong to two different families (Figure 2). The use of ΔH instead of E_b leads to almost identical results (see Supporting Information).

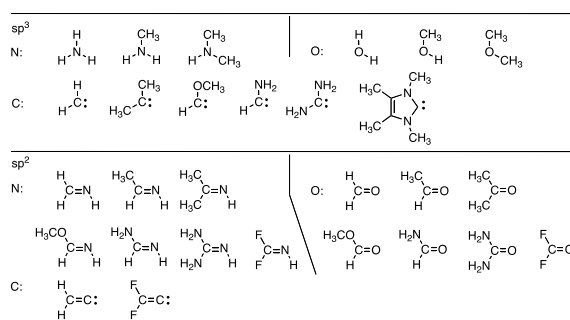


Figure 1. Compounds studied in this work.

The corresponding regression lines are:

$$B = (0.08 \pm 0.07) - (0.009 \pm 0.001) E_b \text{sp}^3, n = 7, R^2 = 0.924, \text{RMS residual} = 0.04$$

$$B = -(0.4 \pm 0.1) - (0.020 \pm 0.002) E_b \text{sp}^2, n = 7, R^2 = 0.954, \text{RMS residual} = 0.06$$

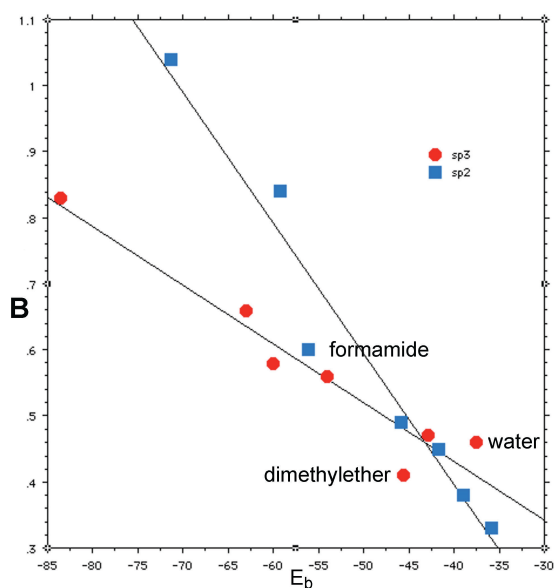


Figure 2. Scattergram of B vs. E_b . Red dots, sp^3 atoms, blue squares, sp^2 atoms. The three out-of-line points are labeled.

The first equation includes Arduengo's carbene (measure 0.83, fitted 0.82). Using these equations we have predicted a number of B values as shown in Table 1.

The fact that sp^2 and sp^3 basic centers are different is probably due to the fact that the calculated E_b values correspond to the gas-phase while the B values have been obtained from solution data. The fact that gas-phase and solution greatly affect basicity is well known.^[28]

We have calculated the minima of the electrostatic potential (MEP) of the eight singlet carbenes in Table 1 to see if there is a correlation with E_b .^[11,29–32] Effectively both magnitudes are related: $E_b = (5.2 \pm 3.5) + (0.24 \pm 0.01) \text{MEP}$, $n = 8$, $R^2 = 0.984$, RMS Residual = $2.6 \text{ kJ} \cdot \text{mol}^{-1}$.

CONCLUSION

Coming back to our initial question about the HBB of carbenes, we have summarized in Figure 3 the results we have obtained.

Figure 3 shows that the most frequent order of hydrogen-bond basicity is $N > C > O$ but that there is a case of $C > N > O$.^[11] Thermodynamic carbon basicity (protonation) is illustrated in a paper about carbon superbases.^[33] In conclusion, carbenes and vinylidenes are, in general, less basic than nitrogen derivatives and, always, more basic than oxygen derivatives, if the structures are similar. On the other hand, hybridization and substituents play an important role on the HBB.

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sp^3	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}: \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}: \\ \\ \text{H}_3\text{C} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{N}-\text{CH}_3 \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{O}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	-54.1 -49.3 -37.5 -68.1 -63.0 -45.6
sp^2	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}=\text{N} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}=\text{C}: \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}=\text{O} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}=\text{N} \\ \\ \text{F} \end{array}$	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}=\text{C}: \\ \\ \text{F} \end{array}$	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}=\text{O} \\ \\ \text{F} \end{array}$	-52.0 -37.7 -35.8 -37.1 -28.3 -20.1

$N > C > O$, $C > N > O$, $N > C > O$, $N > C > O$

Figure 3. Orders of hydrogen-bond basicity.

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Supplementary Information. Atomic coordinates of all molecules in their optimized structures. This material is available free of charge, attached to the electronic version of the article at: <http://doi.org/10.5562/cca3258>.

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