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Behavior of Ylides Containing N, O, and C Atoms as Hydrogen Bond Acceptors

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Abstract: The hydrogen bond (HB) basicity of a series of ylides containing nitrogen, oxygen, or carbon as heavy atoms, as well as the influence of the formation of the HB complexes on their structure, has been studied. In addition, in this paper we propose the formation of some rather strong HBs (that could be considered low-barrier hydrogen bonds, LBHBs) between ylides and different neutral molecules. The ylides chosen for the study were $H_3N^+{-}N^-H$, $Me_3N^+{-}N^-H$, $H_2O^+{-}N^-H$, $Me_2O^+{-}N^-H$, $H_2O^+{-}O^-$, $Me_2O^+{-}O^-$, and $Me_3N^+{-}C^-H_2$. As HB donors, classical donors such as HF, HCN, and HCCH were used. The analysis of the protonation energies of the ylides and the optimized geometries, interaction energies, and characteristics of the electron density of the complexes shows that these ylides are very good HB acceptors, forming stable complexes even with weak HB donors. With strong donors, when the proton transfer did not take place, very strong HBs were formed with quite large interaction energies and very short HB distances which could be considered as LBHBs. Moreover, we have found that the sign of the Laplacian of the electron density at the bond critical point ($\nabla^2\rho_{BCP}$) and that of the energy density (H_{BCP}) could characterize the strength of HBs. Thus, weak HBs (E_I < 12.0 kcal/mol) show both $\nabla^2\rho_{BCP}$ and $H_{BCP} > 0$, and medium HBs ($12.0 < E_I < 24.0$ kcal/mol) show $\nabla^2\rho_{BCP} > 0$ and $H_{BCP} < 0$, while strong HBs (and therefore LBHBs; $E_I > 24.0$ kcal/mol) show both $\nabla^2\rho_{BCP}$ and $H_{BCP} < 0$.

Introduction

Ylides as hydrogen bond (HB) acceptors have been the subject of a number of studies showing a high HB basicity and finding, in some cases, rather strong HB interactions.[1−3] The HB complexes formed with these specific acceptors can show low-barrier hydrogen bond (LBHB) interactions which are particularly short and strong interactions and which have been the focus of a great deal of attention.[4]

Platts and Howard theoretically investigated the ability of N−C or P−C ylides as HB acceptors with C−H donors.[1,2] They found that C−H···C HBs with strengths up to 35 kJ/mol (8.4 kcal/mol) may exist. In the case of the amine and phosphine oxides as HB acceptors, we have previously found that strong HBs (>12 kcal/mol) or medium to strong HBs (∼10 kcal/mol) can be formed with these ylides, even when weak donors such as HCCH were considered.[3] Moreover, when strong acids were used as HB donors, a spontaneous proton transfer was observed.

The stability of ylides has been also extensively studied. As early as 1983, Pople et al. performed a theoretical study of the isomers and rearrangement barriers of "even-electron polyatomic" molecules, such as HNC, H_2NCH, HOCH, H_2NN, H_3NCH_2, H_3NNH, H_3NO, H_2CC, H_3CCH, H_3CN, H_2COH_2, H_2CFH, NOH, $HNOH_2$, HNFH, H_2OO, and HFO, many of which were described as ylide forms.[5] Recently, the stability of the ylide-like intermediate methyleneoxonium (H_2COH_2) has been theoretically studied,[6] the possibility of generating the ylide "oxywater" (H_2OO) has been theoretically calculated at very high levels of computation,[7] and the $R_2O^+{-}O^-$ ylide structures of methanol oxide and dimethyl ether oxide have been theoretically studied as a possible new class of stable ylides.[8,9] Further, the chemical bonding in ylides containing hypervalent atoms has been recently revised by a very accurate analysis of the corresponding electron density at the ylide bond.[9] As well, at the experimental level, the stability of ylides such as H_2CClH, H_2CFH, H_2COH_2, and H_2CNH_3 has been studied by neutralization−reionization mass spectrometry.[10] Moreover, several crystal structures of complexes of hydrazinium and 1,1,1-trimethylhydrazinium have been found in the Cambridge Structural Database[11] which could be considered the result of a proton transfer to the known ylides H_3NNH and Me_3NNH, respectively.

Despite these preexisting findings, most of these ylides have not been studied as HB acceptors, nor have the changes in their electronic nature when the HB complexes are formed been explored. Therefore, the aim of the present paper is to study the HB basicity of a series of ylide molecules containing N, O,

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or C as heavy atoms which have not been previously studied as HB acceptors, and to analyze how the formation of HB complexes affects their ylide structure. Moreover, it has been said that LBHBs would be formed between species when their pK_a values are matched.[4c] In contrast, however, we propose the formation of some rather strong HBs (that could be considered LBHB) between ylides and very different neutral molecules. The ylides chosen for the present study were $H_3N^+{-}N^-H$, $Me_3N^+{-}N^-H$, $H_2O^+{-}N^-H$, $Me_2O^+{-}N^-H$, $H_2O^+{-}O^-$, $Me_2O^+{-}O^-$, and $Me_3N^+{-}C^-H_2$. As HB donors, classical strong, medium, and weak donors such as HF, HCN, and HCCH were used.

Methods

The geometries of the monomers and the complexes have been fully optimized with the program Gaussian 98[12] using the hybrid method Becke3LYP[13] with the standard 6-31G*[14] and 6-311++G**[15] basis sets, and post-Hartree−Fock second-order Møller−Plesset (MP2)[16] calculations with the largest basis set. The nature of the monomers and complexes as a potential energy minimum has been established, at the B3LYP/6-31G*, in all the cases by verifying that all the corresponding frequencies were real.

The interaction energies, $E_I(AB)$, have been calculated as the difference between the energy of the complex and the sum of the energies of the monomers (eq 1):

$$E_I(AB) = E(AB)_{AB} - [E(A)_A + E(B)_B] \qquad (1)$$

where $E(AB)_{AB}$ represents the energy of the complex and $E(A)_A$ the energy of the isolated monomer A calculated with its corresponding basis set.

In addition, a corrected interaction energy (E_{I+BSSE}) excluding the inherent basis set superposition error (BSSE) has been evaluated. The BSSE has been calculated using the Boys−Bernardi counterpoise technique[17] and eq 2:

$$E_{BSSE}(AB) = E(A')_A - E(A')_{AB} + E(B')_B - E(B')_{AB} \qquad (2)$$

where $E(A')_{AB}$ represents the energy calculated for monomer A using its geometry in the complex and the complete set of basis functions used to describe the dimer, and $E(A')_A$ represents the energy for monomer A using its geometry in the complex and its basis set.

The corrected interaction energies (E_{I+BSSE}) have been calculated with eq 3:

$$E_{I+BSSE}(AB) = E_I(AB) + E_{BSSE}(AB) \qquad (3)$$

The topological properties of the electron density at the bond critical points (BCPs) have been characterized using the atoms in molecules (AIM) methodology[18] with the AIMPAC program package[19] at the MP2/6-311++G** level, for the isolated ylides and their HB complexes. The AIM methodology self-consistently partitioned any system and its properties into its atomic fragments, considering the gradient vector field of its electron density distribution. From all the criteria proposed by Koch and Popellier[20] on the basis of the AIMs theory to establish hydrogen bonding, we have chosen the electron density at the bond critical point (ρ_{BCP}), its Laplacian ($\nabla^2\rho_{BCP}$), the atomic charges (N), and the total charge transferred (ΔQ) as the most representative for this kind of interaction. Moreover, since the energy density at the bond critical point (H_{BCP}) has proved to be a more sensible and appropriate index than $\nabla^2\rho_{BCP}$ to characterize the nature of hydrogen bonds,[21] we have also used it in our study. Thus, whereas positive $\nabla^2\rho_{BCP}$ values are usually associated with ionic bonds or HBs, H_{BCP} can become negative in some HBs, which demonstrates the real strength of those bonds.

Results and Discussion

Ylides: Geometry, Energy, and Proton Affinity. The isolated ylides were optimized at the three levels of computation mentioned above, and their MP2/6-311++G** geometries and corresponding total energies are shown in Figure 1. The protonation energy of the ylides studied here (E_{prot}, kcal/mol) was evaluated at the MP2/6-311++G** level, and the results (shown in Table 1) include the B3LYP/6-31G* zero-point vibrational corrections scaled using the factor reported by Rauhut and Pulay[22] calculated for the monomers. The MP2/6-311++G** total energy, the B3LYP/6-31G* ZPE scaled vibrational correction, and the zero-point corrected energies (au) for the monomers and protonated species are gathered as Supporting Information.

In all cases, a large stabilization is observed as a consequence of the protonation (from 209 to 288 kcal/mol). Overall, these ylides can be considered bases of high strength in the gas phase when compared with the experimental protonation affinities of ammonia (204 kcal/mol) and water (165 kcal/mol). The largest protonation energy obtained is that of the $[Me_3N{-}CH_3]^+$ molecule followed by the non-methylated analogue $[H_3N{-}CH_3]^+$ (280 kcal/mol). The protonation energy of those molecules in which the protonated atom is a N atom follows the order $[Me_3N{-}NH_2]^+ > [H_3N{-}NH_2]^+ > [Me_2O{-}NH_2]^+ > [H_2O{-}NH_2]^+$; the protonation energy of those molecules in which the protonated atom is an O atom follows the order $[Me_2O{-}OH]^+ > [H_2O{-}OH]^+$. The less electronegative atoms show the largest protonation energies.

The protonation energy is larger for the methylated ylides ($[Me_nX{-}YH_m]^+$) than for the non-methylated ($[H_nX{-}YH_m]^+$). This increment of protonation energy between the methylated and non-methylated species increases with the electronegativity of the protonated atom ($\Delta E_{prot} = 8$ kcal/mol for $[Z_3N{-}CH_3]^+$

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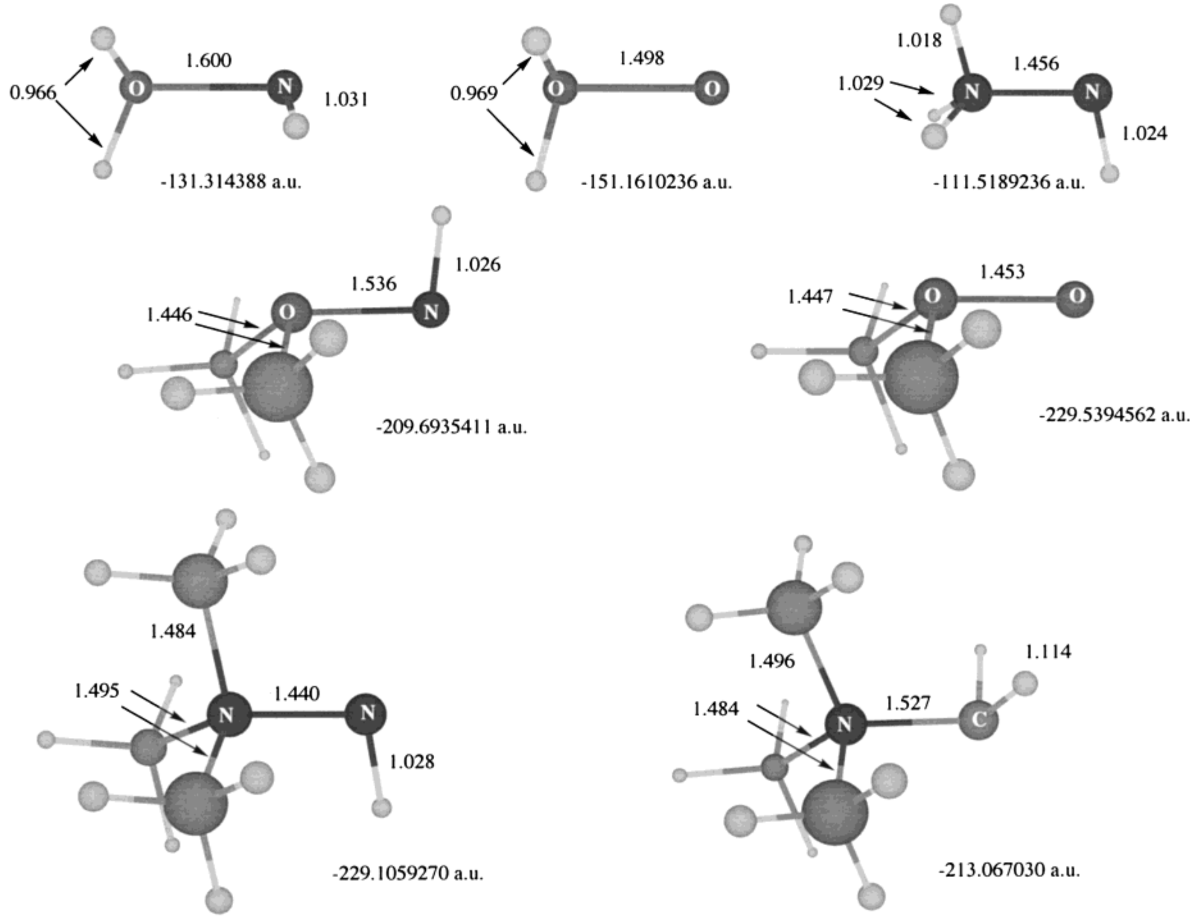

Figure 1. Structures of minimum energy found for the ylides calculated at the MP2/6-311++G** level. Distances in angstroms.

Table 1. Protonation Energy (E_{prot}, kcal/mol) of the Protonated Ylides Calculated at the MP2/6-311++G** Level, Calculated Including the B3LYP/6-31G* Zero-Point Scaled Vibrational Correction (Ref 22)

$X-Y + H^+ \rightarrow [X-YH]^+$	E_{prot}
$H_2O-NH + H^+ \rightarrow [H_2O-NH_2]^+$	236
$H_2O-O + H^+ \rightarrow [H_2O-OH]^+$	209
$H_3N-NH + H^+ \rightarrow [H_3N-NH_2]^+$	251
$H_3N-CH_2 + H^+ \rightarrow [H_3N-CH_3]^+$	280
$Me_2O-NH + H^+ \rightarrow [Me_2O-NH_2]^+$	248
$Me_2O-O + H^+ \rightarrow [Me_2O-OH]^+$	222
$Me_3N-NH + H^+ \rightarrow [Me_3N-NH_2]^+$	262
$Me_3N-CH_2 + H^+ \rightarrow [Me_3N-CH_3]^+$	288

species, $\Delta E_{prot} = 11$ kcal/mol for $[Z_3N-NH_3]^+$ species, $\Delta E_{prot} = 12$ kcal/mol for $[Z_2O-NH_3]^+$ species, and $\Delta E_{prot} = 13$ kcal/mol for $[Z_2O-OH_2]^+$ species).

Hydrogen-bonded complexes can be considered as intermediates in the protonation process. Thus, the gas-phase basicity of a molecule (that is, its stability as a protonated species) could indicate the ability of that molecule to behave as a HB acceptor. Thus, the ylides studied here, in principle, show a very high tendency to form strong HB complexes (very high HB basicity).

Hydrogen-Bonded Complexes: Geometry and Energy. The complexes formed by the non-methylated and methylated ylides and the three HB donors previously mentioned (HF, HCN, and HCCH) were computed at the three levels of theory, and the optimized geometries at the highest level (MP2/6-311++G**) are gathered in Figures 2 and 3, respectively. The MP2/6-311++G** total energy, the B3LYP/6-31G* ZPE scaled vibrational correction, and the zero-point corrected energies (au) for the dimers are gathered as Supporting Information.

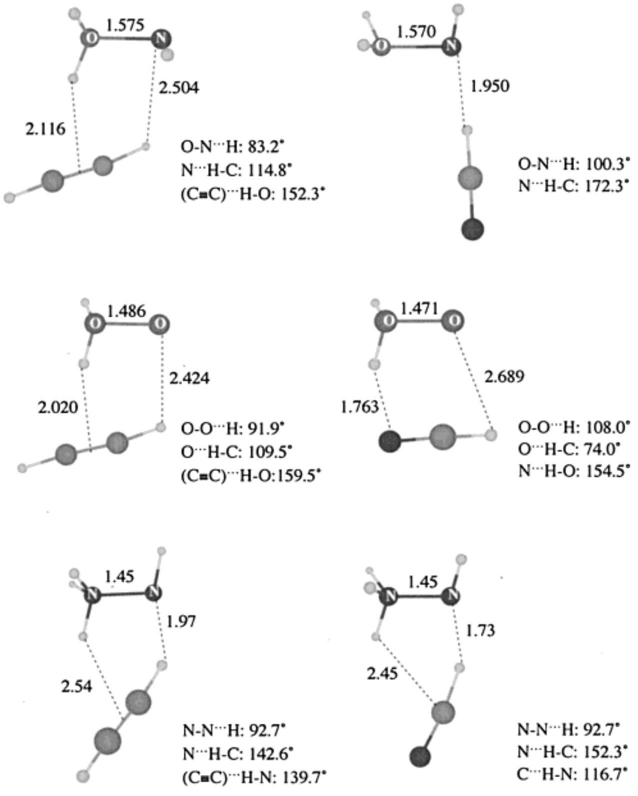

Figure 2. Structures of minimum energy found for the HB complexes with the demethylated ylides calculated at the MP2/6-311++G** level. Distances in angstroms, angles in degrees.

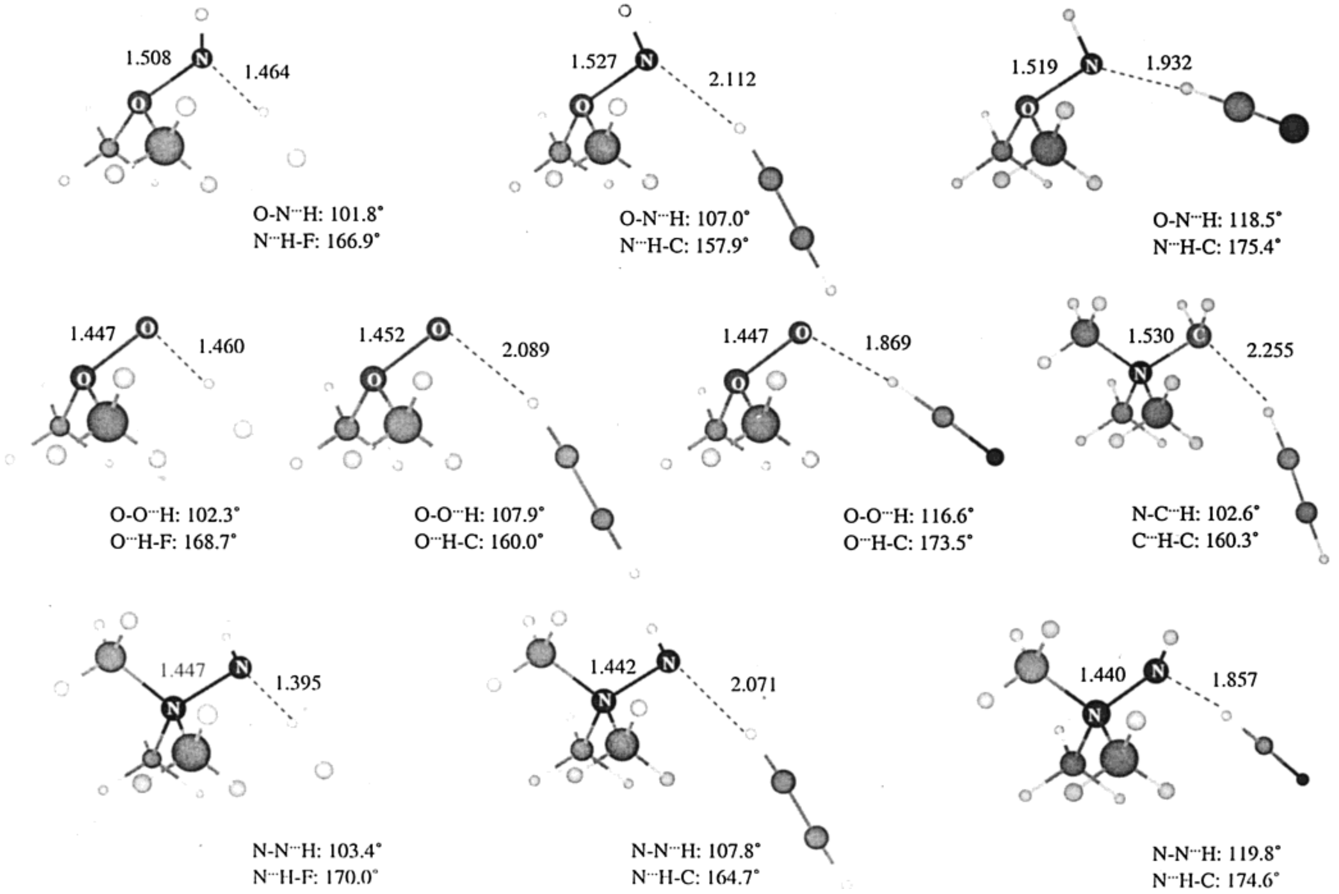

Figure 3. Structures of minimum energy found for the HB complexes with the methylated ylides calculated at the MP2/6-311++G** level. Distances in angstroms, angles in degrees.

In the case of complexes between the non-methylated ylides and HF, a spontaneous double proton transfer between the ylides and the HF occurs. Thus, the HF donates the proton to the δ^- end of the ylide molecule, and this molecule donates a H atom from its δ^+ end to the F^- anion. As a result, it was impossible to obtain, at any level of theory, any HB complex of an ylide with HF as a donor since the spontaneous double proton transfer took place in all cases. Similarly, a single proton transfer also occurred in the case of the Me_3N-CH_2 ylide with both HF and HCN donors. In a previous paper we had observed this kind of spontaneous double proton transfer between amine oxides and HF.[3]

As observed in Figure 2, in the case of the non-methylated ylides, the stationary points found showed several interactions between HB donors and acceptors. These interactions were established not only through the more negatively charged ylide atom, but also by means of the H atoms bonded to the most positively charged ylide atom. Thus, both molecules in the complex were simultaneously acting as HB donors and acceptors, providing cyclic complexes in all cases, except for the $H_2O-O\cdots HCN$ case, where only one possible HB interaction was established. In the complexes with HCCH, a HB interaction with the π-cloud of this molecule was observed.[23]

In the case of the complexes formed by the methylated ylides, only one interaction was established with the HB donors, as can be observed in Figure 3, because the H atoms bonded to the positively charged ylide atom were substituted by CH_3 groups.

The distances obtained (between the H atom of the HB donor and the most negatively charged atom of the ylide; see Figures 2 and 3) were in agreement with HB interactions, except for the case of the $H_2OO\cdots HCN$ complex (2.70 Å), in which the angle around this H atom ($<90°$) confirms that no HB can be established.

Regarding the interaction energies, we report only those results obtained with the largest basis sets (B3LYP/6-311++G** and MP2/6-311++G**), which are shown in Table 2. In this table, both the interaction energy and that corrected by the BSSE effect for all the complexes studied are gathered.

It is known that the BSSE effect is larger for the MP2 calculations than for the B3LYP ones when a TZP basis set is used.[23,24] However, since all the interaction energies are, in general, quite large, corresponding to strong interactions (as expected from this kind of low-barrier HBs), the BSSE effect will not introduce significant qualitative variations as occurs for the case of weak interactions.

AIM Analysis of the Ylides and Their Hydrogen-Bonded Complexes: Atomic Charge, Electron, and Energy Density. The results obtained for the electron density (ρ_{BCP}), its Laplacian ($\nabla^2\rho_{BCP}$), and the energy density (H_{BCP}) at the bond critical points (BCPs) are evaluated by means of the AIM approach at the MP2/6-311++G** level for the isolated ylides and their HB complexes. These are shown in Tables 3 and 4.

The characteristics and changes that occur in the electronic nature of the bond between the two charged heavy atoms in the ylide molecules have been analyzed. The results of the electron density analysis of these ylide bonds, in the isolated molecules and within the HB complexes, are gathered in Table 3. In all the cases the ρ_{BCP} of the ylide bond is larger when this molecule is included in a HB complex, as if the formation of a

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Table 2. Interaction Energies without (E_I, kcal/mol) and with the BSSE Correction (E_{I+BSSE}, kcal/mol) for All the HB Complexes Studied

		B3LYP/6-31G*		B3LYP/6-311++G**		MP2/6-311++G**	
		E_I	E_{I+BSSE}	E_I	E_{I+BSSE}	E_I	E_{I+BSSE}
H_2O-NH	HF	–	–	–	–	–	–
	HCN	−14.5	−10.8	−10.2	−9.1	−11.0	−8.6
	HCCH	−12.4	−8.6	−7.3	−6.7	−8.5	−6.4
H_2O-O	HF	–	–	–	–	–	–
	HCN	−13.3	−9.4	−12.1	−11.4	−12.8	−10.1
	HCCH	−12.7	−8.8	−8.1	−7.6	−9.5	−7.1
H_3N-NH	HF	–	–	–	–	–	–
	HCN	−17.1	−13.5	−12.4	−11.4	−13.4	−10.4
	HCCH	−10.8	−8.1	−8.0	−7.3	−9.7	−7.2
Me_2O-NH	HF	−32.1	−23.2	−21.5	−20.0	−21.2	−16.9
	HCN	−14.0	−11.6	−9.9	−9.3	−11.1	−9.1
	HCCH	−10.1	−7.4	−5.3	−4.7	−7.1	−5.3
Me_2O-O	HF	−30.7	−21.4	−18.4	−17.5	−18.8	−15.1
	HCN	−13.0	−9.8	−8.5	−8.2	−9.5	−7.9
	HCCH	−10.4	−6.9	−4.6	−4.4	−6.4	−4.7
Me_3N-NH	HF	−33.7	−23.5	−26.8	−25.3	−24.6	−20.2
	HCN	−15.3	−12.4	−12.2	−11.7	−13.1	−11.1
	HCCH	−9.4	−6.4	−6.4	−5.9	−8.3	−6.1
Me_3N-CH_2	HF	–	–	–	–	–	–
	HCN	–	–	–	–	–	–
	HCCH	−10.1	−7.2	−6.3	−5.9	−8.2	−6.2

Table 3. Electron Density (ρ_{BCP}, e/au^3), Laplacian ($\nabla^2\rho_{BCP}$, e/au^5), and Energy Density (H_{BCP}, hartrees/au^3) Calculated at the Bond Critical Points of the Ylides, Isolated and within the HB Complexes, at the MP2/6-311++G** Level

X−Y	H−Z	ρ_{BCP}(**X−Y**)	$\nabla_2\rho_{BCP}$(**X−Y**)	H_{BCP}(**X−Y**)
$H_2\mathbf{O}-\mathbf{N}H$	isolated	0.161	0.206	−0.089
	HCN	0.176	0.165	−0.108
	HCCH	0.175	0.164	−0.106
$H_2\mathbf{O}-\mathbf{O}$	isolated	0.222	0.318	−0.128
	HCN	0.244	0.250	−0.155
	HCCH	0.232	0.280	−0.141
$H_3\mathbf{N}-\mathbf{N}H$	isolated	0.269	−0.253	−0.236
	HCN	0.276	−0.294	−0.244
	HCCH	0.273	−0.280	−0.241
$Me_2\mathbf{O}-\mathbf{N}H$	isolated	0.202	0.094	−0.139
	HF	0.221	0.009	−0.166
	HCN	0.213	0.048	−0.155
	HCCH	0.207	0.069	−0.147
$Me_2\mathbf{O}-\mathbf{O}$	isolated	0.260	0.229	−0.177
	HF	0.269	0.177	−0.186
	HCN	0.265	0.202	−0.183
	HCCH	0.262	0.216	−0.178
$Me_3\mathbf{N}-\mathbf{N}H$	isolated	0.288	−0.324	−0.259
	HF	0.287	−0.349	−0.252
	HCN	0.290	−0.345	−0.259
	HCCH	0.287	−0.327	−0.256
$Me_3\mathbf{N}-\mathbf{C}H_2$	isolated	0.203	−0.244	−0.243
	HCCH	0.203	−0.250	−0.242

HB would enforce this particular bond. In addition, this ylide bond becomes slightly shorter (see Figures 1−3), in agreement with the relationships found between the electron density and the bond distance.[25] In general, the increment in density is larger for the non-methylated ylides ($\Delta\rho_{BCP} \approx 0.004-0.022$), forming standard HB or double interaction complexes, than for the methylated ones ($\Delta\rho_{BCP} \approx 0.002-0.019$), in which only standard HB complexes can be formed. Between these methylated ylide complexes, there are some exceptions. For example, in the complex of Me_3N-NH with HF and with HCCH and in the complex of Me_3N-CH_2 with HCCH, the ρ_{BCP} is slightly smaller than or equal to that of the corresponding isolated ylide ($\Delta\rho_{BCP}$ values of −0.001, −0.001, and 0.000, respectively).

Regarding the nature of these ylide bonds, according to the results obtained for the energy density at the BCP (Table 3), they can be considered as covalent bonds in the isolated molecules, in agreement with the results obtained by Molina et al. for the X_2OO derivatives and related structures,[9] as well as within the HB complexes ($H_{BCP} < 0$, always). The sensibility of the H_{BCP} parameter, which provides all negative values, reflects the covalent nature of these bonds compared with the $\nabla^2\rho_{BCP}$, which shows some positive values that could erroneously lead to the conclusion that some of the bonds were "closed-shell" interactions. These kinds of exceptions in the behavior of the Laplacian have been already pointed out.[26]

The electron density analysis of the HB interactions established in these ylide complexes is collected in Table 4. For the non-methylated ylides, only those complexes formed between H_2ONH and H_3NNH with HCN show a unique interaction between the negatively charged atom (N in both cases) and the HB donor. In the case of the $H_2ONH\cdots HCN$ complex, this interaction can be considered as a HB, taking into account the electron density value ($\sim 10^{-2}$ au), the positive values of the Laplacian and the energy density, and the N···H distance (smaller than the sum of the van der Waals radius). However, in the $H_3NNH\cdots HCN$ complex, the electron density is rather large, its Laplacian is positive, the H_{BCP} is negative, and the N···H distance is small. This all indicates the formation of a very strong HB or a LBHB with the ylide.

In the rest of the complexes, the same HB interaction between the negatively charged atom of the ylide molecule and the corresponding HB donor is established (see Table 4). However, a second interaction occurs in which the ylide acts as a HB donor (through the H bonded to the positively charged atom), whereas HCN and HCCH act as HB acceptors (through the N atom of the HCN molecule or through the triple bond of the HCCH molecule; see Figure 2). These secondary interactions should also be considered as HB interactions upon looking at the density values, the positive sign of Laplacians and energy densities, and the corresponding distances (see Table 4). An

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Table 4. Electron Density (ρ_{BCP}, e/au^3), Laplacian ($\nabla^2\rho_{BCP}$, e/au^5), and Energy Density (H_{BCP}, hartrees/au^3) at the Bond Critical Point of the HB Interactions within the Complexes Calculated at the MP2/6-311++G** Level

X−**Y**	**H**−Z	ρ_{BCP}(**Y···H**)	$\nabla^2\rho_{BCP}$(**Y···H**)	H_{BCP}(**Y···H**)	d(**Y···H**)[a]
H_2O−**N**H	HCN	0.030	0.088	0.000	1.950
	HCCH	0.013 (O**H**···(C≡C), 0.022)	0.038 (0.064)	0.001 (0.001)	2.504 (2.116)
H_2O−**O**	**H**CN	0.020 (O**H**···**N**, 0.039)	0.062 (0.108)	0.000 (−0.004)	2.689 (1.763)
	HCCH	0.014 (O**H**···(C≡C), 0.026)	0.045 (0.069)	0.001 (0.000)	2.424 (2.020)
H_3N−**N**H	**H**CN	0.052	0.104	−0.011	1.732
	HCCH	0.029 (N**H**···(C≡C), 0.014)	0.091 (0.053)	0.001 (0.002)	1.975 (2.536)
Me_2O−**N**H	**H**F	0.097	0.073	−0.047	1.464
	HCN	0.032	0.086	−0.001	1.932
	HCCH	0.021	0.069	0.002	2.112
Me_2O−**O**	**H**F	0.085	0.164	−0.031	1.460
	HCN	0.032	0.101	0.000	1.869
	HCCH	0.021	0.066	0.001	2.089
Me_3N−**N**H	**H**F	0.117	−0.001	−0.070	1.395
	HCN	0.038	0.093	−0.003	1.857
	HCCH	0.025	0.070	0.001	2.071
Me_3N−**C**H_2	**H**CCH	0.022	0.046	0.000	2.255

[a] The HB distances (Å), at the same level of calculation, are also included.

Table 5. Electron Density (ρ_{BCP}, e/au^3), Laplacian ($\nabla_2\rho_{BCP}$, e/au^5), and Energy Density (H_{BCP}, hartrees/au^3) Calculated at the Bond Critical Points of Some of the HB Donors, within the HB Complexes, at the MP2/6-311++G** Level

	H−Z−W	ρ_{BCP}	$\nabla_2\rho_{BCP}$	H_{BCP}
Me_2ONH	**H−F**	0.259	−1.486	−0.479
	H−CN	0.264	−0.974	−0.273
	HC≡N	0.455	−0.305	−0.816
Me_2O−O	**H−F**	0.284	−1.821	−0.557
	H−CN	0.268	−0.990	−0.278
	HC≡N	0.455	−0.301	−0.816
Me_3N−NH	**H−F**	0.230	−1.082	−0.385
	H−CN	0.257	−0.937	−0.264
	HC≡N	0.455	−0.312	−0.815

exception is found for the double-bonded H_2OO:::HCN complex, in which the interaction formed between one of the H atoms of the ylide and the N atom of the hydrogen cyanide (see Figure 2) shows negative H_{BCP} and a very short H···N distance, implying a very strong HB.

In the methylated ylide series, a unique interaction was found between the negatively charged atom of the ylide molecules and the HB donors. In all the complexes formed with HCCH, the interaction can be described as a standard HB ($\rho_{BCP} \approx 10^{-2}$ au, $\nabla^2\rho_{BCP}$ and H_{BCP} positive). However, in all the complexes formed with HF, the H_{BCP}'s of the HB interaction were negative, the values of the ρ_{BCP} were very large, and the Y···H distances very short (see Table 4), indicating that the HB interaction is very strong. It could be considered that maybe the proton had already been transferred and that the protonated ylide was interacting with the F atom. However, the electron densities, $\nabla^2\rho_{BCP}$, and H_{BCP} of the corresponding H−F bonds within the complexes (see Table 5) indicate that those are covalent bonds. In the complexes with HCN, both situations are found. The interaction established in the Me_2OO···HCN complex shows ρ_{BCP} around 10^{-2} au, and positive $\nabla^2\rho_{BCP}$ and H_{BCP}, whereas in the complexes with Me_2ONH and Me_3NNH the $\nabla^2\rho_{BCP}$ values are positive and the H_{BCP} values are negative and very small. Again, the electron density characteristics of the bonds of the HCN molecules within the complexes correspond to covalent bonds (see Table 5). Both situations are illustrated in Figures 4 and 5.

Due to the distinctive nature of ylides, which are neutral species with two charged atoms, the variation in their atomic charges when the HB complexes are formed has been studied. The AIM atomic charges for the heavy atoms of the ylides (isolated and within the complexes) and those for the HB donors were computed at the MP2/6-311++G** level of theory and are shown in Tables 6 and 7, respectively.

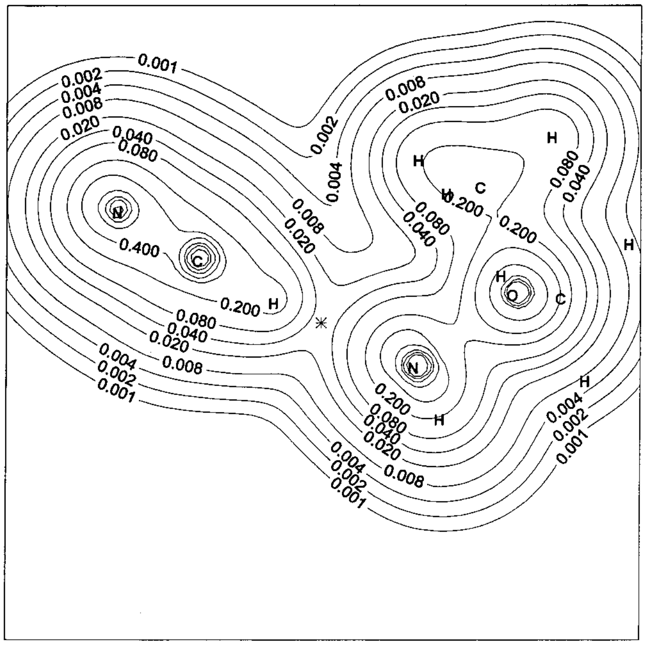

Figure 4. Contour plot of the electron density of the Me_2ONH···HCN complex calculated at the MP2/6-311++G** level.

For the demethylated ylides within the complexes, the negatively charged atom, which is involved in the HB interaction, always suffers an increment of atomic charge, whereas the positively charged atom can increase or decrease the number of electrons when the different interactions are established. When the complexes are formed, the total charge transferred is negative (from the HB donor to the ylide) when double interactions take place and positive (from the ylide to the HB donor) when single HB interactions take place. An exception is the case of the double-bonded H_3NNH:::HCCH complex, when the ΔQ is positive even though two interactions are established. However, in this case the second interaction (between the positively charged N atom and the triple bond of the HCCH molecule) seems to be very weak when looking at the electron density and HB distance.

For the complexes formed between strong HB donors and the methylated ylides, which establish single HB interactions, in general, a decrease in the atomic charge of the interacting atom (the negatively charged) is observed (see Table 6).

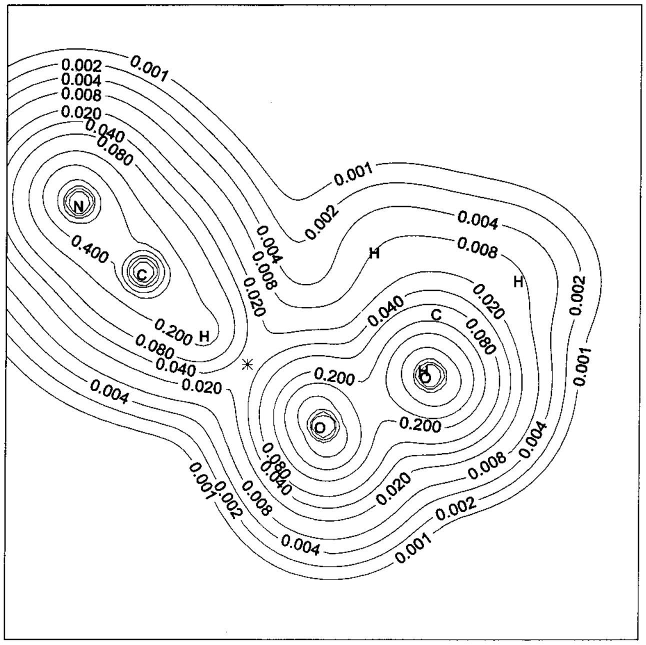

Figure 5. Contour plot of the electron density of the $Me_2OO\cdots HCN$ complex calculated at the MP2/6-311++G** level.

Table 6. AIM Atomic Charges Calculated for the Ylide Atoms in the Isolated Monomers and within the HB Complexes, at the MP2/6-311++G** Level of Theory

X−Y		N(X−)	ΔN(X−)	N(−Y)	ΔN(−Y)
(H_2)**O**−**N**(H)···	isolated	8.928		7.576	
	HCN	8.921	−0.007	7.598	0.022
	HCCH	8.937	0.009	7.588	0.012
(H_2)**O**−**O**···	isolated	8.776		8.499	
	HCN	8.763	−0.013	8.528	0.029
	HCCH	8.781	0.005	8.526	0.027
(H_3)**N**−**N**(H)···	isolated	7.668		7.761	
	HCN	7.682	0.014	7.767	0.006
	HCCH	7.684	0.016	7.774	0.013
(Me_2)**O**−**N**(H)···	isolated	8.815		7.657	
	HF	8.782	−0.033	7.639	-0.018
	HCN	8.801	−0.014	7.670	0.013
	HCCH	8.808	−0.007	7.669	0.012
(Me_2)**O**−**O**···	isolated	8.665		8.547	
	HF	8.629	−0.036	8.528	−0.019
	HCN	8.646	−0.019	8.551	0.004
	HCCH	8.653	−0.012	8.552	0.005
(Me_3)**N**−**N**(H)···	isolated	7.668		7.776	
	HF	7.698	0.030	7.764	−0.012
	HCN	7.679	0.011	7.789	0.013
	HCCH	7.676	0.008	7.779	0.003
(Me_3)**N**−**C**(H_2)···	isolated	7.955		6.101	
	HCCH	7.958	0.003	6.092	−0.009

However, there is no uniformity in these results, since the atomic charge of the ylide atoms varies in each complex without following a pattern. In contrast, in all these complexes, the total charge transferred is always positive (from the HB donor to the ylide) and proportional to the strength of the HB donor. Thus, ΔQ is between 0.098 and 0.160 for the HF complexes, between 0.037 and 0.063 for the HCN complexes, and between 0.013 and 0.046 for the HCCH complexes. Moreover, within each group of a certain HB donor, the ΔQ follows always the same tendency regarding the acceptors: $Me_3NNH > Me_2ONH > Me_2OO$.

Structure−Energy−Electron Density Characteristics Correlations. Some of the complexes studied here show large E_I and ρ_{BCP} ($\sim 10^{-1}$ au) values, short HB distances, and positive $\nabla^2\rho_{BCP}$'s, but negative and small H_{BCP}'s (see Table 4). These last three characteristics have been found as well by other authors (B3LYP/6-31+G**: phosphinic dimer, $d(O\cdots H) = 1.598$, $\rho_{BCP} = 0.051$, $\nabla^2\rho_{BCP} = 0.159$, $H_{BCP} = -0.002$; dimethylphosphinic dimer, $d(O\cdots H) = 1.555$, $\rho_{BCP} = 0.054$, $\nabla^2\rho_{BCP} = 0.167$, $H_{BCP} = -0.003$).[26] Moreover, our results for the $Me_3NNH\cdots HF$ complex show large E_I and ρ_{BCP} values and a short HB distance, but both the Laplacian and the energy density are negative. We have found that the electron density characteristics of the strong HB complex $[F\cdots H\cdots F]^-$ ($E_I \approx 50$ kcal/mol[27]) at the MP2/6-311++G** level are $\rho_{BCP} = 0.174$, $\nabla^2\rho_{BCP} = -0.348$, and $H_{BCP} = -0.206$. Taken together, one may reasonably suggest that these criteria may help characterize HBs. Thus, considering the classification of HBs as weak when the E_I is <12.0 kcal/mol, medium when E_I is between 12.0 and 24.0 kcal/mol, and strong when E_I is >24.0 kcal/mol,[28] we have found that weak HBs show both $\nabla^2\rho_{BCP}$ and $H_{BCP} > 0$, and medium HBs show $\nabla^2\rho_{BCP} > 0$ and $H_{BCP} < 0$, while strong HBs (and therefore LBHBs) show both $\nabla^2\rho_{BCP}$ and $H_{BCP} < 0$ (see Tables 2 and 4).

Table 7. AIM Atomic Charges Calculated for All the Atoms of the HB Donors, Isolated and within the HB Complexes, at the MP2/6-311++G** Level of Theory

		N(···H)	N(**C**)	N(**C**)	N(**H**)	ΔQ[a]
···HCCH	isolated	0.843	6.157	6.157	0.843	
	(H_2)ON(H)···	0.757	6.169	6.215	0.833	−0.026
	(H_2)OO···	0.754	6.160	6.209	0.828	−0.049
	(H_3)NN(H)···	0.702	6.201	6.260	0.854	0.017
	(Me_2)ON(H)···	0.732	6.191	6.237	0.857	0.017
	(Me_2)OO···	0.741	6.191	6.227	0.854	0.013
	(Me_3)NNH···	0.714	6.198	6.259	0.862	0.033
	$(Me_3)NCH_2$···	0.719	6.196	6.269	0.862	0.046

		N(···H)	N(C)	N(N)	ΔQ[a]
···HCN	isolated	0.779	5.231	7.990	
	(H_2)ON(H)···	0.674	5.264	8.101	0.039
	(H_2)OO···	0.755	5.096	8.130	−0.019
	(H_3)NN(H)···	0.617	5.333	8.122	0.072
	(Me_2)ON(H)···	0.666	5.279	8.105	0.050
	(Me_2)OO···	0.673	5.271	8.093	0.037
	(Me_3)NNH···	0.642	5.298	8.123	0.063

		N(···H)	N(F)	ΔQ[a]
···HF	isolated	0.288	9.712	
	(Me_2)ON(H)···	0.317	9.813	0.130
	(Me_2)OO···	0.292	9.806	0.098
	(Me_3)NNH···	0.344	9.816	0.160

[a] The total charge transferred is also given.

Some authors have described a certain relationship between the E_I's of HB complexes and the corresponding proton affinities.[4c,29] We have found that, considering independently the different HB donors, the trends in the E_I's follow that of the methylated ylides' E_{prot}'s. That is, there is a direct relationship between the size of the E_I of a complex and the E_{prot} of the corresponding ylide ($Me_3NNH > Me_2ONH > Me_2OO$).

Other relationships that have been used widely in the study of HB complexes ($RX\cdots H{-}YP$) are those described between the E_I's and the XY or XH distances. However, we have found that the E_I of our complexes correlates better with the XH/XY ratio. This XH/XY parameter not only represents the distance between the heavy atoms involved in the HB interaction (XY) or the distance of the HB interaction itself (XH) but also, by considering the ratio between both distances, includes a certain

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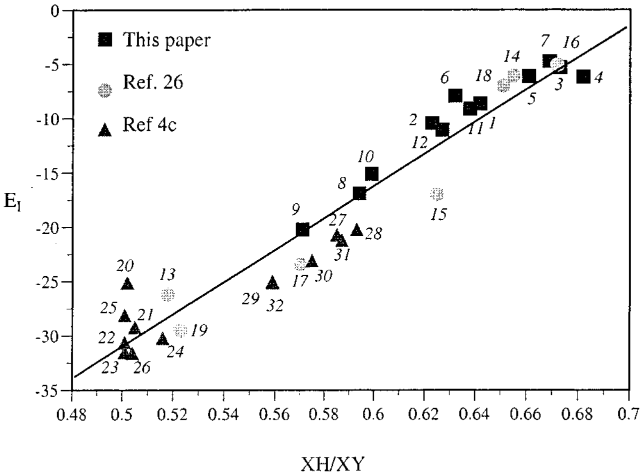

Figure 6. Calculated interaction energies (E_I, kcal/mol) as a function of the XH/XY ratio of distances calculated for a series of RX···H−YP complexes. Represented by squares, complexes calculated in this paper at the MP2/6−311++G** level: **1**, H_2ONH···HCN; **2**, H_3N-NH···HCN; **3**, Me_2ONH···HCCH; **4**, Me_3NCH_2···HCCH; **5**, Me_3NNH···HCCH; **6**, Me_2OO···HCN; **7**, Me_2OO···HCCH; **8**, Me_2ONH···HF; **9**, Me_3NNH···HF; **10**, Me_2OO···HF; **11**, Me_2ONH···HCN; **12**, Me_3-NNH···HCN. Represented by circles, complexes calculated in ref 23 at the MP2/6-31++G** level: **13**, $HCOO^-$···HOOCH; **14**, HC-OOH···HOOCH; **15**, $HCOO^-$···HOH; **16**, HCOOH···HOH; **17**, $(H_2O)HCOO^-$···HOOCH; **18**, (H_2O)HCOOH···HOOCH; **19**, (H_2O)HC-OO^-···HOOCH(H_2O). Represented by triangles, complexes calculated in ref 4c at the MP2/6−31+G** level: **20**, MeCOOH···$^-$OOCMe; **21**, CH_2FCOOH···$^-OOCCH_2F$; **22**, CHF_2COOH···$^-OOCCHF_2$; **23**, CF_3CO-OH···$^-OOCCF_3$; **24**, FCOOH···$^-$OOCF; **25**, OHCOOH···$^-$OOCOH; **26**, CNCOOH···$^-$OOCCN; **27**, HCOOH···$^-$OOCF; **28**, HCOOH···$^-$OOCCN; **29**, HCOOH···$^-OOCCH_2F$; **30**, HCOOH···$^-OOCCHF_2$; **31**, HCOOH···$^-OOCCF_3$; **32**, HCOOH···$^-$OOCOH.

correction for the possible angle of this interaction since ∠(X···H−Y) would not necessarily be 180°. To extend this correlation to the case of LBHBs, we include in our equation some E_I's and distances (calculated at the MP2/6-31+G** level) from a series of formic acid−formate anion dimers taken from the literature.[4c,30] The linear correlation obtained is represented in Figure 6, and the corresponding equation,

$$E_I = -106.001 + 149.589(XH/XY)$$
$$r^2 = 0.94,\ n = 32,\ SD = 2.37$$

demonstrates a sufficiently good regression coefficient taking into account the differences in the systems compared.

Other regressions were tested, such as E_I vs d(XH) or E_I vs d(XY). However, their results were worse than that of E_I vs XH/XY. These distance variables have been used by many other authors to explain the strength of HBs.

Besides, the introduction of a second independent variable (the X···H−Y angle) was tested only for the set of complexes calculated in this paper. Yet, this second variable did not improve greatly the regression coefficient:

$$E_I = -98.248 + 138.898(XH/XY)$$
$$r^2 = 0.92,\ n = 12,\ SD = 1.41$$

$$E_I = -106.347 + 141.963(XH/XY) + 0.037(X\cdots H-Y)$$
$$r^2 = 0.93,\ n = 12,\ SD = 1.46$$

Conclusions

Ylides are very good HB acceptors, forming very stable HB complexes with quite large E_I's, even with weak HB donors such as HCCH (from −4.7 to −7.2 kcal/mol). With strong HB donors such as HF, when the proton transfer did not take place, very strong HBs were formed, with E_I's between −15.1 and −20.2 and very short HB distances (between 1.39 and 1.46 Å). This kind of very strong and short HBs is also found in some of the complexes with HCN.

Taking into account the E_I's and E_{prot}'s computed and the total charge transferred when the complexes are formed (ΔQ), it is possible to order the methylated ylides by their strength as HB acceptors. Therefore, even though all of them are very good HB acceptors, Me_3NNH seems to be better than Me_2ONH, which is better than Me_2OO.

Moreover, we have found that, as the E_I of a complex increases, the E_{prot} of the corresponding ylide increases. Therefore, the order of strength within each family of HB donors was always $Me_3NNH > Me_2ONH > Me_2OO$.

With respect to the electron density characteristics obtained for the complexes studied, we suggest that these criteria can be used to characterize HBs. Thus, we have found that weak HBs show both $\nabla^2\rho_{BCP}$ and $H_{BCP} > 0$, and medium HBs show $\nabla^2\rho_{BCP} > 0$ and $H_{BCP} < 0$, while strong HBs (and therefore LBHBs) show both $\nabla^2\rho_{BCP}$ and $H_{BCP} < 0$.

Regarding the correlations found, the fact that the XH/XY ratio correlates better with the E_I than the HB distance (XH) or the distance between heavy atoms (XY) is interesting. It seems that the HB distance alone does not explain the strength of the bond because even though X···H is very short, the H−Y distance can be elongated, resulting in a weak interaction. Moreover, the XY distance, in principle, could better reflect the interaction between HB donor and acceptor. However, since the X···H−Y moiety is not necessarily linear, d(XY) could not be fully representative of the HB interaction. Nevertheless, the XH/XY ratio expresses the proportion of the HB bond with respect to the distance between both HB donor and acceptor systems. This gives a more representative idea of the HB interaction, and probably for that reason correlates better with the E_I, which reflects the strength of the HB.

By looking at the regression represented in Figure 6, it is possible to differentiate the normal HBs (upper part of the plot) from those which are considered LBHBs (lower part of the plot). Thus, complexes **13**, **17**, and **19**−**32** calculated by Pan and McAllister[30] and defined by them as LBHBs appear in the same area as complexes **8**, **9**, and **10**, which are those formed by Me_2-ONH, Me_3NNH, and Me_2OO with HF, in agreement with our conclusions.

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Supporting Information Available: Tables of total energy, B3LYP/6-31G* ZPE scaled vibrational correction, and zero-point corrected energies for the protonated species, the monomers, and the dimers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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