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Theoretical Study of the Symmetry of the $(OH\cdots O)^-$ Hydrogen Bonds in Vinyl Alcohol−Vinyl Alcoholate Systems

Asit K. Chandra[†] and Thérèse Zeegers-Huyskens*[,†,‡]

Birla Institute of Technology and Science, Pilani 333 031, Rajasthan, India, and Department of Chemistry, University of Leuven, 200F Celestijnenlaan, 3001 Heverlee, Belgium

therese.zeegers@chem.kuleuven.ac.be

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The interactions between substituted vinyl alcohols and vinyl alcoholates (X = NH_2, H, F, Cl, CN) are studied at the B3LYP/6-311++G(d,p) level of theory. In a first step, the conformation of the monomers is investigated and the proton affinities (PA(A^-)) of the enolates are calculated. The enols and enolates are held together by strong $(OH\cdots O)^-$ hydrogen bonds, the hydrogen bond energies ranging from 19.1 to 34.6 kcal mol^{-1}. The optimized O···O distances are between 2.414 and 2.549 Å and the corresponding OH distances from 1.134 and 1.023 Å. The other geometry parameters such as C═C or CO distances also indicate that, in the minimum energy configuration, the hydrogen bonds are characterized by a double well potential. The Mulliken charges on the different atoms of the proton donors and proton acceptors and the frequencies of the ν(OH) stretching vibrations agree with this statement. All the data indicate that the hydrogen bonds are the strongest in the homomolecular complexes. The transition state for hydrogen transfer is located with the transition barrier estimated to be about zero. Upon addition of the zero-point vibration energies to the total potential energy, the barrier vanishes. This is a characteristic feature of low-barrier hydrogen bonds (LBHBs). The hydrogen bond energies are correlated to the difference 1.5 PA(AH) − PA(A^-). The correlation predicts different energies for homomolecular hydrogen bonds, in agreement with the theoretical calculations. Our results suggest that a PA (or pK_a) match is not a necessary condition for forming LBHBs in agreement with recent data on the intramolecular hydrogen bond in the enol form of benzoylacetone (*J. Am. Chem. Soc.* **1998**, *120*, 12117).

Introduction

These past few years there has been growing interest in the nature of short-strong or low-barrier hydrogen bonds (LBHBs). In a monodimensional approach, a hydrogen bond can be defined as an LBHB if the ground vibrational level of the double well lies at or above the classical barrier, according to the definition given by Cleland and Kreevoy.[1] The study of these hydrogen bonds has recently revived because of their presumed role during enzyme catalysis.[2a−l] Cleland and Kreevoy discussed the special stabilization arising from hydrogen bonding between proton donors and acceptors at matched pK_a and suggested that the requirement for forming LBHBs appears to be the absence of a hydrogen bonding solvent such as water and similar pK_a values of the two heteroatoms involved in the bond.[1] As shown in a recent work,[2m] however, LBHBs do form in hydrogen bonding solvents

As pointed out by Perrin,[3] if the two acceptors are identical, it might naively be thought that the hydrogen bond must be symmetric so that the hydrogen bond would not need to choose which acceptor it will be closer to. Nevertheless, both situations have been observed even with identical acceptor atoms.

Experimental and computational studies have demonstrated a relationship between the increase of hydrogen bond strength and the decrease in the difference in pK_a (ΔpK_a) or the difference in proton affinity (ΔPA) of the two molecules or ions which share the proton.[4]

The relationship between hydrogen bond strength and ΔPA is, in general, only approximately linear and the deviation from linearity increases when the hydrogen donor and acceptor abilities become very different.[5] The Marcus equation, although not valuable for high-barrier hydrogen bonds, also implies a nonlinear dependence of the correlation between the hydrogen bond strength and ΔPA.[6] These correlations are useful for predicting hydrogen bond strengths in large clusters or biomolecules. Substantial deviations from these correlations may also suggest special structural effects such as double hydrogen

[†] Birla Institute of Technology and Science.
[‡] University of Leuven.

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bonding. However, the intrinsic basicity or acidity of the two partners are not the sole factors determining the hydrogen symmetry or strength. This is clearly suggested by the following features.

1. While the best hydrogen acceptor for AH is A^-, it is not generally possible to predict the relative strength of $(AH\cdots B_1)^-$ and $(AH\cdots B_2)^-$ based on the ΔpK_a values or ΔPA values of B_1 and B_2 relative to A. It can happen that the gas-phase hydrogen bond strength of $(AH\cdots B_1)^-$ is smaller than that of $(AH\cdots B_2)^-$ even though the ΔPA is smaller in the former. The main reason is that the slopes of the linear equations correlating the hydrogen bond strength and ΔPA strongly depend on the nature of the corresponding hydrogen bonds. For a variety of nonsymmetrical $(OH\cdots O)^+$, $(NH\cdots O)^+$, and $(SH\cdots O)^+$ systems, slopes ranging from 0.16 up to 0.43 have been observed.[4d,e,h]

2. Further, as discussed in a recent work,[7] the pK_a or PA match criterion cannot be used to predict the relative strength of homomolecular hydrogen bonds belonging to different families such as $(HOH\cdots OH)^-$ or $(ClH\cdots Cl)^-$. The same remark also holds in complexes where the proton is shared between two neutral molecules. Even in closely related homomolecular hydrogen bonds such as $(R_2O\cdots H\cdots OR_2)^+$, the hydrogen bond strength depends on the nature of the R substituent, decreasing with the PA of R_2O.[8]

The present work deals with a theoretical study of the hydrogen bond complexes formed between substituted vinyl alcohols and vinyl alcoholates $(XHC{=}CHOH\cdots OHC{=}CHY)^-$ (X, Y = NH_2, H, F, Cl, CN). The systems are formed by different combinations of the monomers leading to 5 homomolecular (X = Y) and 10 homonuclear (X ≠ Y) complexes. The corresponding $(OH\cdots O)^-$ hydrogen bonds are expected to be strong. Some of these complexes have been theoretically investigated at the Hartree−Fock (HF) level combined with the 6-31G(d) basis set.[9] This level, however, does not predict accurate PA values of the monomers and hydrogen bond geometries or energies.[10] In the present work, the calculations are carried out at the B3LYP/6-311++G(d,p) level. As shown recently, density functional methods combined with an extended basis set should be reliable for the study of LBHB systems.[11]

In most of the papers related to LBHBs, only one specific system is investigated. The main objective of this work is to investigate, in these closely related complexes, the variation of the hydrogen bond energies with the geometry parameters and with the proton donating or accepting abilities of the interacting species. The charge shifts resulting from complex formation are analyzed as well. In the first section, we discuss relevant properties of the isolated vinyl alcohols and their anions.

Computational Methods

All computations reported here were performed with the density functional hybrid B3LYP potential[12,13] in conjunction with the split-valence 6-311++G(d,p) basis set. The geometries of isolated vinyl alcoholds and vinyl alcoholates and their complexes were fully optimized without any constraints. Harmonic vibrational frequencies were kept unscaled. The proton affinities of the anions defined as the negative of the enthalpy change for the gas-phase reaction $A^- + H^+ \rightarrow AH$ were calculated at the same level. The interaction energies were determined as the difference in energy between the complex, on one hand, and the sum of the isolated monomers, on the other hand. These energies were corrected for the zero-point vibrational energies (ZPE). The basis-set superposition error correction is small (0.3 kcal mol^{-1} for the (H,H) complex) and was therefore not taken into account.

The Gaussian 98 package of programs[14] was used for all the calculations reported in the present work. All data refer to the standard conditions of 1 atm and 298 K.

Results and Discussion

Selected Properties of Vinyl Alcohol and Vinyl Alcoholate Monomers. In this section, we will briefly discuss some selected properties of the vinyl alcohol and vinyl alcoholate monomers which are relevant for the study of their complexes. As discussed in a previous work,[15] the syn conformation of vinyl alcohol is preferred over the anti one. Ab initio calculations carried out at the MP2/6-31G(d)//6-31G level have shown that the anti conformer is less stable by 2.07 kcal mol^{-1} than the syn conformer.[15b] The value of 1.39 kcal mol^{-1} calculated in the present work does not differ markedly from this value but is in better agreement with the experimental value of 1.08 kcal mol^{-1}.[15] In the substituted vinyl alcohols, the X substitutent can be in the cis or trans position. This

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CHART 1

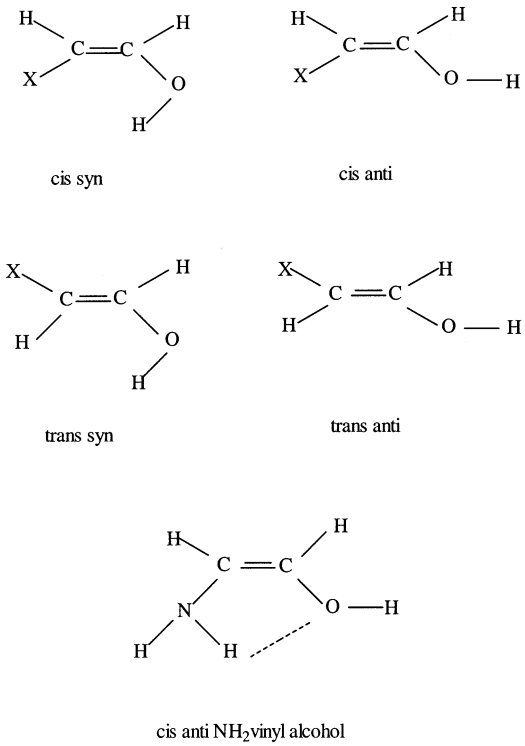

TABLE 1. Relative Energies of the A, B, C, and D Conformers of Substituted Vinyl Alcohols and Proton Affinities of the Corresponding Vinyl Alcoholates (in kcal mol^{-1})

X	cis-syn	cis-anti	trans-syn	trans-anti
		relative energies		
NH_2	0	1.09	4.78	5.01
H	0	1.39		
F	0	3.42	4.08	4.48
Cl	0	3.63	3.95	4.80
CN	0	3.39	2.15	2.72
		proton affinities (PA^-)		
NH_2	353.0	352.2	352.4	352.2
H	350.4	349.1	-	-
F	347.5	344.2	344.6	344.2
Cl	342.0	338.5	339.2	338.5
CN	326.1	322.9	321.9	321.4

leads to 4 different conformations, displayed in Chart 1. Their relative energies are reported in Table 1. In all the derivatives, the cis-syn conformation is preferred over the other conformations. The cis-anti conformer appears to be relatively more stable than the two trans conformers. However, in the CN-vinyl alcohol, the two trans structures appear to be slightly more stable than the cis-anti one. We may note also that the cis-syn NH_2-vinyl alcohol may be stabilized by a weak intramolecular NH···O hydrogen bond, as displayed in Chart 1. This is suggested by the (N)H···O distance of 2.455 Å, which is smaller than the sum of the van der Waals radii of the H and O atoms (2.60 Å).

The PAs were calculated for protonation constrained onto oxygen. The PAs corresponding to the different conformers of the vinyl alcoholates are reported in Table 1. These results indicate that the PAs of the most stable cis-syn conformers are sligthly larger than the PAs of the other conformers. It is also worth noticing that the calculated PA of the most stable conformer of vinyl alcoholate, which must largely predominate in the gas phase, is equal to 350.4 kcal mol^{-1}. This value is in good agreement with the experimental value of the gas-phase acidity of 355 ± 3 kcal mol^{-1},[16a] and with the calculated B3LYP/6-31+G(d,p) value of 352.5 kcal mol^{-1}.[16b] The PA of vinyl alcoholate calculated at the HF/6-31G(d) level is equal to 377 kcal mol^{-1},[9] larger than the experimental value by more than 20 kcal mol^{-1}. This shows that reliable values of PA can only be obtained when adding diffuse functions on non-hydrogen atoms.[17] Owing to the change in hybridization at the C bonded to O and the high polarizability of the π-bonds, the acidity of the vinyl alcohol is expected to be higher than that of methanol.[16b] No calculated or experimental data are available for the PAs of the other vinyl alcoholates. It is noteworthy that in the gas phase, CN-vinyl alcohol is more acidic than 4-NO_2 phenol (PA of the corresponding anion = 328.2 kcal mol^{-1}),[16a] which is very often taken as the model proton donor in hydrogen bond studies.

TABLE 2. Selected B3LYP/6-311++G(d,p) Geometrical Parameters of Cis-Anti Vinyl Alcohols and Cis-Vinyl Alcoholates (Bond Lengths in Å, Bond Angles in Deg)

	X parameter				
	NH_2	H	F	Cl	CN
		vinyl alcohols			
r(O−H))	0.9605	0.9606	0.9605	0.9609	0.9619
r(C=C)	1.336	1.328	1.328	1.330	1.342
r(C−O)	1.388	1.370	1.364	1.360	1.348
∠C=C−O	119.7	122.3	123.0	123.5	122.7
		vinyl acoholates			
R(C=C)	1.377	1.384	1.369	1.376	1.406
R(C−O)	1.278	1.267	1.267	1.258	1.246
∠C=C−O	128.2	130.4	132.5	132.8	130.2

Inspection of the results of Table 2 shows that the PAs of the vinyl alcoholates are ordered as follows, NH_2 > H > F > Cl > CN, which is consistent with the order predicted by the theory of substituent effects.[18]

Table 2 reports selected geometry parameters for isolated vinyl alcohols and vinyl alcoholates. These parameters refer to the cis-anti conformers in the vinyl alcohols and to the cis conformers in the vinyl alcoholates which are the only relevant ones in the corresponding complexes where $(OH\cdots O)^-$ hydrogen bonds between the neutral molecules and their anions are formed. The main objective of this work is to discuss the geometries and energetics of the complexes; therefore, only these conformers will be considered hereafter. We may also note that the trans conformation considered in ref 9 does not correspond to the minimum energy structure in the isolated molecules as well as in their complexes.

Our results indicate that the O−H bond is slightly more elongated in Cl- and CN-vinyl alcohol. This is in

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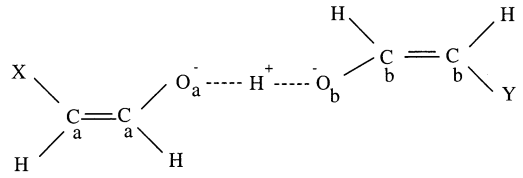
CHART 2



good agreement with the smaller deprotonation enthalpies predicted for these molecules. The C=C bonds do not show regular variation with the substituent in the neutral molecules; they are shorter by ca. 0.04−0.05 Å in the corresponding anions. The most sensitive bond to substitution and to deprotonation is the C−O bond. Indeed, the C−O bond length decreases from 1.388 to 1.348 Å on going from NH_2- to CN-vinyl alcohol. In the anions, this bond length decreases further from 1.278 to 1.246 Å. This can be accounted for by an increase of the delocalization of the oxygen lone pairs into the C−O bond, which increases with the electron-accepting power of the substituent and which must be obviously larger in the negatively charged compounds.

Deprotonation of the enol also results in geometry changes in the C≡N or NH_2 substituents. The C≡N distance is equal to 1.157 Å in the neutral enol and increases up to 1.168 Å in the corresponding anion. The particular geometry of the NH_2 group is also worth mentioning. As shown by the NH_2 angle equal to 112° and by the sum of the angles around the N atom equal to 340.7°, the amino group has a strong pyramidal character in the neutral molecule. This pyramidal character is even more pronounced in the corresponding anion where the NH_2 angle and the sum of the angles around the N atom take values of 104° and 320°, respectively, which indicates a nearly sp^3-hybridized N atom.

Geometry of the Vinyl Alcohol−Vinyl Alcoholate Complexes. The schematic structure of the complexes formed by different combinations of monomers is indicated in Chart 2. Selected optimized geometry parameters are reported in Table 3. It should be noted that the HF ab initio approaches overestimate the O···O separation by more than 0.1 Å. In the (X = NH_2, Y = CN) complex, the O···O distance predicted by the HF method combined with the 6-31G(d) basis set is equal to 2.71 Å,[9] larger by 0.16 Å than the distance of 2.55 Å calculated in the present work. This is certainly due to the inclusion of electron correlation, which is neglected at the HF level. The role of diffuse functions in the basis set is also important for the proper representation of long-term attractive forces.

Our results show that the enol and enolate C=C bonds do not lie in the same plane, one plane being slightly tilted from the other plane, but that may not be very important for our purpose. In all the studied systems, the asymmetrical structure where $r(O_aH) < r(O_bH)$ is a true minimum. The departure from linearity is weak, the $O_aH\cdots O_b$ angle ranging from 175.1° to 178.7°. The O···O distances are the shortest, between 2.414 and 2.428 Å for the homomolecular complexes. The elongation of the O_aH bond resulting from the interaction with the anions ranges between 0.156 and 0.181 Å and is also the largest for these complexes. It also must be noticed that in the homolecular complex formed between formic acid and the formate anion, calculations carried out at a comparable level (B3LYP/6-31++G(d,p) have predicted the lowest energy for an asymmetrical structure, the O···O and O_aH distances being equal to 2.432 and 1.172 Å, respectively,[19] very similar to the data reported in the present work.

TABLE 3. Selected Geometrical Parameters of the Minimum Energy Structures in Substituted Vinyl Alcohol−Vinyl Alcoholate Complexes (Bond Lengths in Å, Bond Angles in Deg.)

X	Y	$r(O_aH)$	$r(HO_b)$	$\angle O_aHO_b$	$R(O\cdots O)$
NH_2	NH_2	1.117	1.311	178.7	2.427
NH_2	H	1.106	1.331	178.5	2.441
NH_2	F	1.080	1.378	178.1	2.457
NH_2	Cl	1.053	1.438	177.6	2.490
NH_2	CN	1.023	1.527	177.0	2.549
H	H	1.120	1.308	178.3	2.428
H	F	1.087	1.365	177.8	2.450
H	Cl	1.057	1.428	177.1	2.482
H	CN	1.027	1.516	176.3	2.542
F	F	1.142	1.274	178.0	2.414
F	Cl	1.074	1.388	176.4	2.461
F	CN	1.043	1.489	175.1	2.521
Cl	Cl	1.132	1.287	177.8	2.418
Cl	CN	1.046	1.452	175.6	2.497
CN	CN	1.134	1.280	177.5	2.414

X	Y	$r(C-O)_a$	$r(C-O)_b$	$r(C=C)_a$	$r(C=C)_b$
NH_2	NH_2	1.331	1.311	1.348	1.355
NH_2	H	1.333	1.300	1.347	1.361
NH_2	F	1.337	1.296	1.345	1.352
NH_2	Cl	1.342	1.284	1.343	1.359
NH_2	CN	1.349	1.267	1.341	1.387
H	H	1.317	1.301	1.351	1.360
H	F	1.322	1.296	1.349	1.351
H	Cl	1.326	1.285	1.346	1.359
H	CN	1.333	1.268	1.333	1.387
F	F	1.313	1.303	1.343	1.348
F	Cl	1.322	1.288	1.340	1.357
F	CN	1.329	1.270	1.337	1.385
Cl	Cl	1.307	1.294	1.349	1.353
Cl	CN	1.320	1.272	1.341	1.383
CN	CN	1.295	1.283	1.366	1.375

The results of Table 3 allow one to establish a correlation between the $r(O_aH)$ distances and the distances between the heavy atoms, displayed in Figure 1. The best fit is found for the following second-order polynomial:

$$r(O_aH) = 5.1\,R(O\cdots O)^2 - 26.31R(O\cdots O) + 34.79 \quad (r = 0.9958) \quad (1)$$

Most sophisticated correlations between the OH and O···O distances have been proposed by Gilli et al.[20] Nevertheless, eq 1 is characterized by an excellent correlation coefficient of 0.9958. It is worth mentioning that this equation predicts a symmetrical $(OH\cdots O)^-$ hydrogen bond for $r(OH)$ and $R(O\cdots O)$ values equal to 1.19 and 2.38 Å, respectively. These values are very similar to the experimental values obtained from neutron diffraction data[20] showing that the shortest OH···O hydrogen bonds characterized by O···O distances of 2.39 Å display more or less perfectly centered protons typical of the symmetrical O···H···O geometry. Equation 1 also can be

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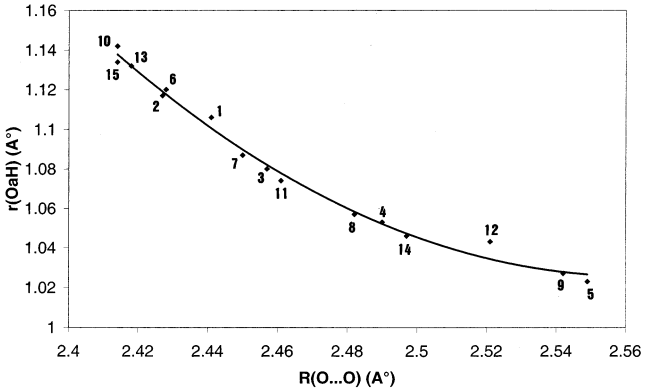

FIGURE 1. $r(O_aH)$ (Å) as a function of $R(O\cdots O)$ (Å). The numbers refer to the following complexes: (1) (NH_2,NH_2); (2) (NH_2,H), (3) (NH_2,F), (4) (NH_2, Cl), (5) (NH_2,CN), (6) (H,H), (7) (H,F), (8) (H,Cl), (9) (H,CN), (10) (F,F), (11) (F,Cl), (12) (F,CN), (13) (Cl,Cl), (14) (Cl,CN), (15) (CN,CN).

extended to weaker and more asymmetrical hydrogen bonds. For the OH distance of 1 Å, this equation allows one to predict the O···O distance of 2.60 Å, which is in very good agreement with the experimental curve displayed in ref 20.

The asymmetry of the OH···O hydrogen bond in its minimum energy structure is also reflected by the intramolecular $(C-O)_a$ and $(C-O)_b$ distances and by the $(C=C)_a$ and $(C=C)_b$ distances which are intermediate between the distances predicted in the isolated enols, on one hand, and the distances in the isolated enolates, on the other hand. Also, in the homomolecular complex (NH_2,NH_2), the geometry parameters of the NH_2 group are not equivalent, the NH_2 angle being equal to 107.4° in the neutral molecule and 106.4° in the anion. We note also an increase of this angle up to 108.5° in the homonuclear (NH_2,CN) complex. It is also worth mentioning that the N(H)···O intramolecular bond is sligthly strengthened in the complexes. In the (NH_2,H) system, for example, the intramolecular (N)H···O distance is equal to 2.380 Å, shorter by 0.075 Å than the corrresponding distance of 2.455 Å in the isolated molecule. This can be accounted for by an increase of the charge on the O_a atom, thus reinforcing its proton acceptor ability. The existence of this intramolecular interaction is also demonstrated by slightly different Mulliken charges on the two hydrogen atoms of the NH_2 group which are equal to 0.23e in the bridge H and 0.19e in the free H.

Energies of the Vinyl Alcohol−Vinyl Alcoholate Complexes. The hydrogen bond energies (E_{HB}) and the ZPE corrections for the 15 stable complexes investigated in the present work are reported in Table 4. This table also contains the hydrogen bond energies of complexes, where the acidic proton is bonded to the anion having the lowest PA ($\Delta PA < 0$). Starting from the free O_aH, O_b^-, and H^+ species, one can consider the reaction paths (a) and (b).

$$O_aH\cdots O_b^- \overset{(a)}{\Leftarrow} O_a^- + H^+ + O_b^- \overset{(b)}{\Rightarrow} O_a^-\cdots HO_b$$

The hydrogen bond energies correspond to the association via path (a) when the basicity of O_a^- is higher than that of O_b^- ($\Delta PA > 0$); in this case, the proton is preferentially bonded to O_a^-. One can also consider the association via path (b), where the proton is bonded to the anion having the lowest PA ($\Delta PA < 0$). The association energies for these metastable complexes must differ from the energies of the most stable complexes by the difference in PA of the two partners. Our results are in conformity with these expectations, the small differences being due to numerical rounding effects.

The data reported in Table 4 indicate that the hydrogen bond energies vary within a broad range, from 19.1 to 34.6 kcal mol^{-1}. Except for the (F,H) and (Cl,F) systems which are more stable by less than 1 kcal mol^{-1} than the (NH_2,NH_2) system, the largest energies are obtained for the homomolecular complexes. It is very important to note that the energies in these systems are not constant but drop from 34.6 to 27.3 kcal mol^{-1} by going from the most acidic proton donor (X = CN) to the least acidic one (X = NH_2).

In none of the complexes could the transition state be optimized. This implies for all the complexes a very shallow double minimum well with a very small activation energy ($E_A \approx 0$) for proton transfer. As shown by the data of Table 4, the potential energy barrier for proton transfer including the ZPE-contribution takes values between −0.07 and −1.54 kcal mol^{-1} for all the complexes except for the homomolecular and the (H,NH_2) ones. Thus, all these complexes can be categorized as LBHBs. The ground vibrational state appears to be slightly above the classical energy barrier. Similar theoretical results carried out at a comparable level (B3LYP/6-31++G(d,p)) have been obtained for the PA-matched complex between formic acid and the formate ion where $E_A = 0$ and $E_A + ZPE = -0.27$ kcal mol^{-1}.[19] Also, in a Kemp's triacid monoanion, where intramolecular $(OH\cdots O)^-$ hydrogen bonds stabilize the structure, the DFT results yield a potential curve for proton transfer involving two minima, the equilibrium OH distances being 1.13 and 1.29 Å, respectively. The O···O distance in the transition state is shorter by 0.03 Å than the minimum energy distance. The classical energy barrier is only 0.06 kcal mol^{-1}, a vanishingly small value, and the ZPE contribution is equal to −2.3 kcal mol^{-1}.[21] It is also worth mentioning that for homomolecular complexes, the ZPE contributions are slightly positive, varying from 0.05 to 0.49 kcal mol^{-1}. If the homonuclear complexes can be categorized as LBHBs, this is certainly the case for the homomolecular complexes which are characterized by smaller intermolecular distances and larger binding energies. The origin of these unexpected results will be discussed in a forthcoming paper.[22]

There has been considerable discussion regarding hydrogen bond strength and length.[20] There is, however, scarce experimental evidence for it.[23] Hibbert and Emsley have compared the experimental energies of OH···O hydrogen bonds with the O···O distances found in crystal structures for a limited number of compounds.[24] They have shown that the energies of the OH···O hydrogen

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TABLE 4. B3LYP/6-311++G(d,p) Hydrogen Bond Energies (in kcal mol^{-1}, Including ZPE Contributions) for the Vinyl Alcohol−Vinyl Alcoholate Complexes[a]

	X				
Y	NH_2	H	F	Cl	CN
NH_2	27.31 (0.05)	29.76 (0.07)	33.51 (−0.46)	36.95 (−0.84)	48.38 (−1.42)
H	26.74 (−0.16)	29.42 (0.07)	32.97 (−0.07)	36.24 (−0.94)	47.48 (−1.54)
F	25.53 (−0.61)	28.01 (−0.54)	32.80 (0.25)	33.72 (−069)	44.45 (−1.44)
Cl	23.17 (−0.85)	25.48 (−0.86)	27.93 (−0.56)	33.03 (0.17)	41.58 (−1.12)
CN	19.14 (−1.06)	21.26 (−1.10)	23.18 (−0.95)	26.02 (−0.77)	34.61 (0.49)

[a] The underlined values refer to complexes where the proton is transferred to the enolate bearing the Y substituent. The ZPE contributions to the hydrogen bond energies are indicated in parentheses.

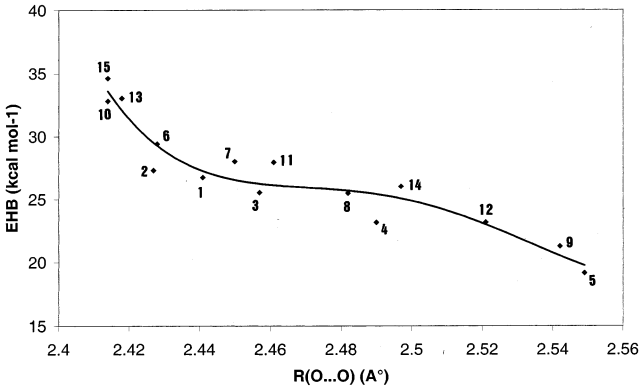

FIGURE 2. E_{HB} (kcal mol^{-1}) as a function of R(O···O) (Å). Same numbering as in Figure 1.

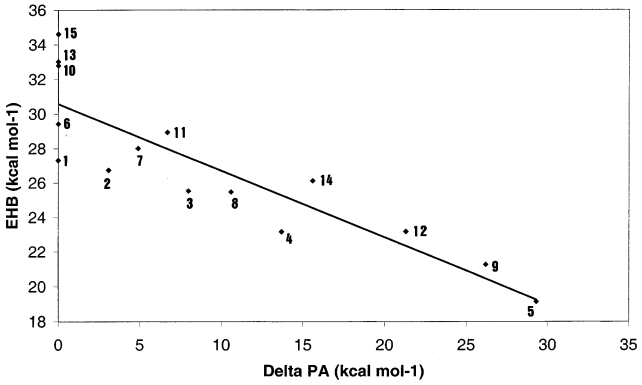

FIGURE 3. E_{HB} (kcal mol^{-1}) as a function of ΔPA (kcal mol^{-1}). Same numbering as in Figure 1.

bonds change dramatically around 2.45 Å. Quantum-mechanical and semiempirical calculations also indicate there is a functional dependence between hydrogen bond energy and the O···O distance, the latter increasing almost exponentially when the O···O distance tends to its minimum.[25] Figure 2 displays the correlation between E_{HB} and R(O···O) for the present complexes. This figure indicates that there is a smooth increase of the energies when the O···O distances become shorter. There appears to be a slight but not spectacular upward curvature of this plot as the geometries approach 2.45 Å.[26,27]

Correlation between Hydrogen Bond Energies and PAs. As outlined in the Introduction, numerous correlations between the experimental or calculated hydrogen bond energies and differences in the PAs of the two partners have been established in the literature. However, very few quantitavive correlations have been established for LBHBs. For the interaction between formic acid and substituted formate anions, the differences in calculated E_{HB} correlate roughly with the calculated differences in PAs. The introduction of the CN substituent causes an approximately 7 kcal mol^{-1} decrease in E_{HB}, the difference in PAs being 16 kcal mol^{-1}.[19] The results of ref 19 clearly show that the introduction of any substituent leads to a decrease in the calculated E_{HB}. It must be observed, however, that for the complex between formic acid and the CH_3-formate (acetate) anion, there is an apparent increase of the E_{HB} calculated at the HF level. This may be accounted for by the fact that this complex is metastable, the minimum energy structure corresponding to that of the acetic acid−formate anion complex.

In the present complexes, both the X and Y substituents are allowed to vary. The difference between the PAs of NH_2- and CN-vinyl alcoholate is equal to ca. 29 kcal mol^{-1}. This corresponds to differences in E_{HB} equal to ca. 8 kcal mol^{-1} for the (NH_2,Y) series and ca. 14 kcal mol^{-1} for the (CN,Y) series which include the metastable complexes. Excellent correlations are obtained between E_{HB} and the PAs of the anions, if the proton donor is held constant. The slopes and intercepts of the five correlations obtained in this way are not constant but increase with the acidity of the proton donor. To obtain reliable data in the five systems, we have compared in a first step the calculated E_{HB} for the stable systems with the difference in PAs (ΔPA = PA(AH) − PA(A$^-$)) of the two partners. The correlation illustrated in Figure 3 shows relatively poor precision. The corresponding equation can be written as:

$$E_{HB} = 30.57 - 0.386\Delta PA \quad (\Delta PA \geq 0;\ r = 0.8795) \tag{2}$$

This equation predicts the same E_{HB} values for the 5 homomolecular complexes. This is not in agreement with the fact that the calculated interaction energies in the (NH_2,NH_2) and (CN,CN) systems differ by more than 7 kcal mol^{-1}. The intercept of eq 2 represents approximately the average of the hydrogen bond energy in the five homomolecular complexes. As outlined in the previous section, the binding energy is the largest in the (CN,CN) complex where the proton acceptor is character-

(25) Lippincott, E. R.; Schroeder, R. *J. Chem. Phys.* **1955**, *23*, 1099.
(26) The best mathematical fit is the following fourth order polynomial: $E_{HB} = -6877.5R(O\cdots O)^4 + 51270R(O\cdots O)^3 - 127413R(O\cdots O)^2 + 105567R(O\cdots O)$ ($r = 0.9448$). We have some doubt about the general character of this equation, which predicts much too large hydrogen bond energies for symmetrical hydrogen bonds. In ref 27, a fourth order polynomial along with other coeffiecients have been proposed.
(27) Grabowski, S. J.; Krykowski, T. M. *Tetrahedron* **1998**, 5683.

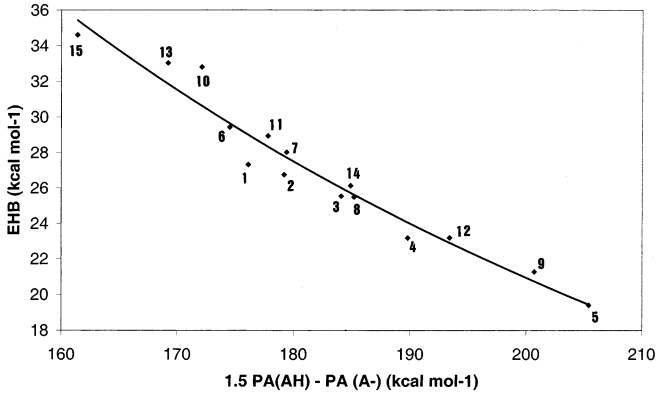

FIGURE 4. E_{HB} (kcal mol^{-1}) as a function of 1.5 PA(AH) − PA(A$^-$) (kcal mol^{-1}). Same numbering as in Figure 1.

ized by the highest acidity and the proton acceptor by the smallest basicity. This finding also is in very good agreement with the fact that in formally symmetric proton-held dimer cations $(BHB)^+$, the hydrogen bond energies decrease as the PA of the base increases.[8] These consideractions strongly suggest that better correlations between the hydrogen bond energies and differences in PAs of the two partners can be obtained when taking different coefficients for the proton donor and the proton acceptor. We must also note that for alcohol−alkoxide clusters, different coefficients for the proton donor and proton acceptor have been proposed by Caldwell.[28]

For the present complexes, the best correlations are obtained when taking coefficients of the PA of the proton donor and the proton acceptor equal to 1.5 and 1, respectively. The following linear equation is obtained:

$$E_{HB} = 95.53 - 0.360[1.5\mathrm{PA(AH)} - \mathrm{PA(A^-)}] \quad (r = 0.9695) \quad (3)$$

However, in a relatively broad range, the correlation must be nonlinear since E_{HB} approaches zero for large ΔPA.[5d] For the present complexes, a sligthly better correlation coefficient is found for the following exponential expression:

$$E_{HB} = 318.2e^{-0.0136[1.5\mathrm{PA(AH)}-\mathrm{PA(A^-)}]} \quad (r = 0.9806) \quad (4)$$

We note that both eqs 3 and 4 predict different binding energies for the homomolecular complexes. However, as illustrated in Figure 4, the curve for these complexes shows strong curvature, which is what accounts for the discrepancy. To discuss this point in more detail, more experimental or theoretical data for homomolecular complexes will be necessary. It is also worth mentioning that the greater importance of the proton donor in determining the hydrogen bond energies has been recently outlined for the interaction between nucleobases and water[29] and seems to be a general feature of the hydrogen bond.

TABLE 5. Mulliken Charges on the O_a, H, and O_b Atoms and Charge Transfer (in e) and Frequencies of the ν(OH) Vibration (in cm^{-1}) in Selected Vinyl Alcohol−Vinyl Alcoholate Complexes[a]

(X,Y)	O_a	H	O_b	CT	ν(OH)
(NH_2,CN)	−0.46 (+0.16)	+0.49 (−0.22)	−0.45 (0.00)	0.08	2670
(H,Cl)	−0.40 (+0.18)	+0.47 (−0.22)	−0.48 (−0.04)	0.12	2150
(F,Cl)	−0.43 (+0.20)	+0.49 (−0.24)	−0.48 (−0.04)	0.14	1950
(NH_2,NH_2)	−0.58 (+0.28)	+0.63 (−0.37)	−0.62 (+0.09)	0.13	1245
(H,H)	−0.45 (+0.22)	+0.50 (−0.24)	−0.52 (−0.01)	0.18	1125
(F,F)	−0.48 (+0.25)	+0.51 (−0.26)	−0.53 (−0.03)	0.20	—[b]
(Cl,Cl)	−0.41 (+0.20)	+0.53 (−0.25)	−0.46 (−0.06)	0.18	1035
(CN,CN)	−0.37 (+0.18)	+0.54 (−0.26)	−0.42 (−0.04)	0.18	1040

[a] The values in parentheses indicate the variations of the charges with respect to the corresponding isolated vinyl alcohols or vinyl alcoholates. The "+" sign indicates a gain of electronic density and the "−" sign a loss of electronic density. [b] Strongly mixed mode.

The question arises if eq 4 allows one to predict the hydrogen bond strength in other $(OH\cdots O)^-$ systems. We may find the answer to this question by considering the clustering reactions of hydroxide or aliphatic alkoxides. In this case also, the largest energies are obtained when ΔPA tends to zero.[30] The experimental hydrogen bond energies in the $(HOH\cdots OH)^-$ and $(CH_3OH\cdots OCH_3)^-$ clusters are equal to 26.8 and 28.8 kcal mol^{-1}, respectively. The PA values of OH^- and CH_3O^- are 390.7 and 381.6 kcal mol^{-1}. Thus eq 4 predicts, for these systems, hydrogen bond energies which are equal to 22.3 and 23.8 kcal mol^{-1}, respectively. These values are lower than the experimental energies by 4.5−5 kcal mol^{-1}. These considerations indicate that even for $(OH\cdots O)^-$ hydrogen bonds, no general correlation between hydrogen bond strengths and PAs can be found. Even for closely related complexes, the coefficients of the exponential expression depend intimately on the nature of the interacting molecules. In the vinyl alcohols, the weakening of the hydrogen bond results, at least partly, from charge delocalization in the partners.[30] Other effects such as steric interactions should also be taken into account.[7]

The results of the present work show that the PA-match may not be the only determining factor for establishing LBHBs. This has also been demonstrated for the intramolecular OH···O hydrogen bond in benzoylacetone where the hydrogen bond is slightly asymmetrical even in the transition state.[2k] In this case, we can roughly estimate the PA-mismatch from the PAs of the parent molecules such as acetone (PA = 196.7 kcal mol^{-1}) and acetophenone (PA = 205.4 kcal mol^{-1}). The deprotonation enthalpies of the corresponding enols are 369.5 and 362.5 kcal mol^{-1}, respectively.[16a] Therefore, the PA-mismatch may be of the order of 7 to 9 kcal mol^{-1}.

Mulliken Charges and Frequencies of the OH Stretching Vibration. Table 5 contains, for selected systems, the Mulliken charges on the O_a, H, and O_b atoms, the variation of the charges induced by complex formation, along with the overall charge transfer taking place from the anion to the neutral molecule. In all the systems, complex formation results in a gain of electronic density on the O_a atom and a loss of electronic density on the H forming the bridge, leading to an increased polarization of the O_a−H bond. This is a general feature

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(29) (a) Chandra, A. K.; Nguyen, M. T.; Zeegers-Huyskens, Th. *J. Phys. Chem. A* **1998**, *102*, 6010. (b) Chandra, A. K.; Nguyen, M. T.; Uchimaru, T.; Zeegers-Huyskens, T. *J. Phys. Chem. A* **1999**, *103*, 8853. (c) Kryachko, E. S.; Nguyen, M. T.; Zeegers-Huyskens, Th. *J. Phys. Chem. A* **2001**, *105*, 3379.

(30) Meot-Ner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1986**, *108*, 7525.

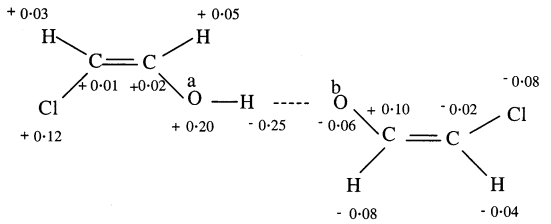

FIGURE 5. Charge shifts (e) resulting from hydrogen bonding formation in the (Cl,Cl) complex. The "+" sign indicates a gain of charge and the "−" sign a loss of charge.

of the hydrogen bond. There is also (except in the NH_2 complexes) a very small decrease of charge on the O_b atom. The charge transfer, larger than the sum of the variations of the charges on the atoms forming the bridge, is spread over the whole complex. One example of charge shifts is shown in Figure 5 for the (Cl,Cl) complex.[30] The two H atoms and the Cl atom of the enolate lose electronic charges and there is also a marked gain of charge on the carbon atom attached to the O, leading to an increasing polarization of the enolate. A great deal of the charge is transferred to the electronegative Cl atom of the enol. The charge transfer is larger for the homomolecular complexes and a rough correlation between charge transfer and hydrogen bond energies is observed.

The asymmetry of the hydrogen bond in the homomolecular complexes is again reflected by the different charges on the O_a and O_b atoms. It is also worth mentioning that large atomic partial atomic charges are found on the oxygen atoms on the hydrogen atom involved in the interaction. This suggests that a substantial electrostatic interaction is present in these strong hydrogen bonds. As for the intramolecular hydrogen bond in benzoylacetone,[2k] this does not exclude a covalent component as well, as originally proposed by Gilli et al.[20]

One of the most characteristic features of the hydrogen bond is the frequency decrease of the ν(OH) stretching vibration, which usually parallels the elongation of the OH bond. In the free enols, the ν(OH) frequencies are calculated between 3868 and 3855 cm^{-1}. Table 5 contains the ν(OH) frequencies for some selected complexes. These values should be taken with caution since they are based on a harmonic model. Furthermore, the ν(OH) vibrations calculated at frequencies lower than 1500 cm^{-1} appear to be coupled with the $\delta(OHO)^-$ deformation vibrations. Our results show nevertheless that for the weakest interactions, the ν(OH) frequencies are predicted around 2650 cm^{-1}. These frequencies decrease with increasing strength of the hydrogen bond. In the five homomolecular complexes, the ν(OH) frequencies are calculated between 1240 and 1030 cm^{-1}. It is worth mentioning that the experimental ν(OH) frequencies in intermolecular OH•• •...O hydrogen bonds characterized by a single minimum potential are observed at lower frequencies, between 750 and 850 cm^{-1},[31] in full agreement with the data presented in the present work.

Conclusions. In this work, the interaction between 15 complexes formed between vinyl alcohols and vinyl alcoholates is investigated at the B3LYP/6-31++G(d,p) level of theory. The hydrogen bonds are strong, their energies ranging from 19.1 to 34.6 kcal mol^{-1}. The main results emerging from our analysis are the following ones.

1. The geometry parameters, Mulliken charges, and vibrational frequencies demonstrate that the minimum energy structure corresponds to an asymmetrical hydrogen bond. The barrier to proton transfer is negligibly small and becomes negative after ZPE corrections, in the homonuclear systems. These results indicate that the investigated $(OH\cdots O)^-$ hydrogen bonds can be categorized as LBHBs, the homomolecular hydrogen bonds being the strongest ones.

2. Numerous correlations between the hydrogen bond strength and ΔPA have been presented in the literature. These correlations predict identical hydrogen bond energies at matched-PA. The present work suggests that better correlations are obtained when considering the difference 1.5PA(AH) − PA(A^-) instead of ΔPA.

3. The correlations between the distances, hydrogen bond strengths, and PAs are not linear, but there is no discontinuity of the curves for the homomolecular hydrogen bonds.

4. The PA-match may not be the only determining factor for establishing LBHBs.

JO020735H

(31) Mulliken charges on all the atoms and vibrational frequencies can be obtained from the authors, on request.

(32) Novak, A. *Stuct. Bonding* **1974**, *18*, 177.