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LCAO-MO-SCF-Calculations on the Stability and Sterochemistry of Hydrogen Bonds*

VI. LCAO-MO-Calculation on Molecular Structure**

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CNDO and INDO calculations were performed on numerous structures with hydrogen bonds of different strength. An almost linear relationship is found between the strength of weak hydrogen bonds and the amount of charge transfered. π-electrons and lone pairs are nearly equivalent in hydrogen bonding. The stereochemistry of hydrogen bonds is determined largely by additional interactions between σ-bonds of the two molecules. Since proton affinities are calculated too large by the CNDO method, an error is introduced in the potential curves for proton transfer in weak hydrogen bonds. In systems with strong hydrogen bonds both structures with the proton on the right and left have almost the same energy and hence the potential curves for proton transfer are free of the errors mentioned above.

Strukturen mit Wasserstoffbrücken unterschiedlicher Stärke wurden mit Hilfe der CNDO- und INDO-Methode berechnet. In Systemen mit schwachen Wasserstoffbrücken wird ein fast linearer Zusammenhang zwischen der Brückenenergie und der Ladungsübertragung gefunden. π-Elektronen und einsame Elektronenpaare sind nahezu gleich gut zur Ausbildung von Wasserstoffbrücken geeignet. Die Stereochemie von Wasserstoffbrücken wird darüber hinaus weitgehend von der Wechselwirkung zwischen den übrigen σ-Bindungen in beiden Molekülen bestimmt. Da Protonenaffinitäten mit der CNDO-Methode zu groß berechnet werden, sind die Potentialkurven für den Protontransfer in schwachen Wasserstoffbrücken mit einem Fehler behaftet. In starken Wasserstoffbrücken weisen die beiden Strukturen mit dem Proton rechts oder links vergleichbare Energien auf, und die Potentialkurven sind deshalb frei von den erwähnten Fehlern.

Calculs CNDO et INDO sur de nombreuses structures avec des liaisons hydrogène de forces différentes. Une relation presque linéaire est obtenue entre la force des liaisons hydrogène faibles et la quantité de charge transférée. Les électrons π et les paires libres jouent un rôle presque équivalent dans la liaison hydrogène. La stéréochimie des liaisons hydrogène estlargement déterminée par les interactions additionnelles entre les liaisons σ des deux molécules. La méthode CNDO donnant des affinités protoniques trop élevées, une erreurs s'introduit dans les courbes de potentiel pour le transfert du proton dans les liaisons hydrogène faibles. Dans les systèmes à liaisons hydrogène fortes les deux positions du proton donnent des structures d'énergies presque égales et les courbes de potentiel ne sont pas entachées des erreurs précédentes.

Introduction

Hydrogen bonding is of fundamental importance in chemistry and molecular biology and has been studied extensively by both theoretical and experimental methods. Recently Bratoz [1] reviewed the different theoretical approaches

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towards an understanding of the hydrogen bond. Some progress was achieved during the last two years, when semiempirical and *ab initio* LCAO–MO–SCF-methods were applied to this subject by several groups [2–7]. Most frequently Pople's CNDO procedure [8–10] was used. The results of CNDO/2 calculations — electron distribution and interaction energies — were compared with *ab initio*-LCAO–MO–SCF calculations and experimental data [4–6]. The CNDO method turned out to be appropriate for a "semi-quantitative" description of hydrogen bonded structures.

The stereochemistry of hydrogen bonds had been discussed only in few papers [11–13]. Since the angular dependence of the interaction energy is of great importance in many fields we calculated energy surfaces for the usual types of hydrogen bonds in detail. In order to save computation time the smallest molecules showing the essential properties were chosen: HF, H_2O, H_3N, formaldehyd and pyridine.

The relation between the energy of proton transfer and the stability of the hydrogen bond is of general interest. The starting point for every description of nuclear motion is the potential surface of the electronic energy. Therefore we calculated potential curves for proton transfer in weak and strong intermolecular hydrogen bonds. Proton affinities of small molecules and anions were calculated and compared with experimental data in order to test the reliability of the CNDO potential curves.

Method of Calculation and Results

The CNDO method developed by Pople and coworkers [8–10] was used to calculate the electronic structures and energies of our model systems. The mathematical formalism used is the same as described in the original papers, CNDO/2 [10] and INDO [14]. Calculations were performed for the structures with hydrogen bonds ($Y \cdots H{-}X$) and the isolated molecules. For the purpose of comparison the total energy of the isolated molecules is taken as zeropoint of the energy scale:

$$\Delta E_{HB} = -\{E(Y \cdots H{-}X) - (E_Y + E_{HX})\}\,. \tag{1}$$

In order to be able to compare our results with those of other groups all parameters of the CNDO- and INDO-method were taken unchanged from the original papers [10, 14]. The calculations were performed on an IBM 7040 (Aerodynamische Versuchsanstalt, Göttingen) and an IBM 360/44 computer (Institut für Statistik, Universität Wien). Modified versions of the QCPE[1] programs 91 and 141 were used.

The energies of the interacting molecules were minimized by the following procedure:

1. The energies of the isolated molecules were minimized and the "CNDO/2-molecular-geometries" were used as a starting point for subsequent calculations. In the case of formaldehyde and pyridine, which can only act as proton acceptors, the experimental geometries were used (Table 1).

2. Energy curves were calculated for the approach of the two molecules with the atoms X, H and Y lying on a straight line. The curves obtained show

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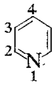
[1] Quantum chemistry program exchange, Bloomington, Indiana.

Table 1. *Geometries of the isolated molecules used in the* CNDO- *and* INDO-*calculations*

Molecule	Geometry	Origin
H–F	$R_{HF} = 1.004$ Å	1
	$R_{HF} = 1.006$ Å	2
H_2O	$R_{HO} = 1.03$ Å	1
	$<HOH = 107.1°$	
H_3N	$R_{HN} = 1.066$ Å	1
	$<HNH = 106.7°$	
H_2CO	$R_{HC} = 1.12$ Å	3
	$R_{CO} = 1.21$ Å	
	$<HCH = 120°$	
	$R_{HC} = 1.08$ Å	3
	$R_{NC_2} = 1.34$ Å	
	$R_{C_2C_3} = 1.39$ Å	
	$R_{C_3C_4} = 1.40$ Å	
	$<CNC = 116°$	
	$<NCC = 124°$	
	$<C_2C_3C_4 = 120°$	

1: CNDO/2 energy minimum,
2: INDO energy minimum,
3: exp. values [19].

energy minima in the range of $2.4 < R_{XY} < 2.8$ Å. When the distance between the molecules is increased, the energy and the charge distribution reach continuously the values for infinite separation. Hence the one determinantal wave function of the semiempirical LCAO–MO–SCF method is appropriate for a description of hydrogen bonding.

3. At the energy minimum of the distance between the two heavy atoms (R_{XY}) the bond length R_{HX} is varied. In the case of systems with weak hydrogen bonds the new energy minimum is almost identical with the total energy minimum of the surface $E(R_{HX}, R_{XY})$. No subsequent variation of the distance R_{XY} was necessary, cf. also [4].

In systems with strong hydrogen bonds, e.g. $[F\cdots H\cdots F]^-$, $[HO\cdots H\cdots OH]^-$, $[H_2O\cdots H\cdots OH_2]^+$, the symmetrical structures, $R_{HX} = R_{HY}$, were minimized directly and afterwards proved to be the energy minimum by small deviations from symmetry.

The results obtained are summarized in Table 2. The ΔE_{HB} values are somewhat larger than those reported by Kollman and Allen [5], because they kept the experimental geometries of the monomers constant and did not approach the CNDO energy minima.

4. It is known from previous calculations on systems with intermolecular hydrogen bonds, that a deviation from the linear arrangement of the three atoms $Y\cdots H–X$ leads to an increase in energy. Therefore we performed exclusively calculations on the other type of angular dependence shown in Fig. 1. The angles ω and ϑ were varied at fixed distances R_{HX} and R_{XY}. Systematic calculations were performed with the HF molecule as proton donor. Because of its linearity

Table 2. *Calculated distances and energies in structures with hydrogen bonds (linear arrangement, $\omega = 0°$, $\vartheta = 0°$)*

Molecules or ions		CNDO/2-calculations				Charge transfer
Y	H–X	R_{YX} (Å)	R_{HX} (Å)	ΔR_{HX} (Å)	ΔE_{HB} (kcal/mole)	$\Delta q(e_0)$
H_2CO	$H–NH_2$	2.72	1.071	0.005	3.6	0.017
H_2O	$H–NH_2$	2.69	1.075	0.009	4.5	0.019
H_3N	$H–NH_2$	2.74	1.080	0.014	5.8	0.032
H_2CO	H–OH	2.55	1.04	0.01	7.2	0.039
H_2O	H–OH	2.54	1.04	0.01	8.7	0.036
HF	H–F	2.44	1.010	0.006	9.4	0.041
H_3N	H–OH	2.58	1.05	0.02	11.2	0.059
H_2CO	H–F	2.44	1.017	0.013	13.2	0.061
H_2O	H–F	2.42	1.020	0.016	15.4	0.064
	H–F	2.46	1.030	0.026	19.4	0.093
H_3N	H–F	2.46	1.030	0.026	20.0	0.097
H_2O	$H–OH_2^+$	2.34	1.17	0.14	59.7	0.289
HO^-	H–OH	2.34	1.17	0.14	72.2	0.365
F^-	H–F	2.25	1.125	0.121	102.1	0.350
		INDO-calculation				
H_2CO	H–F	2.36	1.031	0.024	21.2	0.100

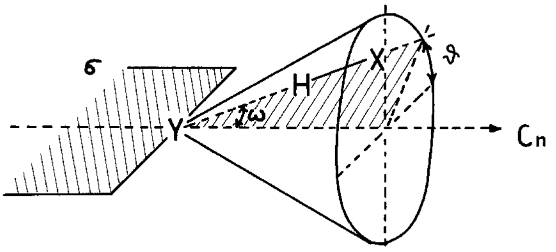


Fig. 1. Coordinates for the description of angular dependence of hydrogen bonds (C_n...n-fold symmetry axis of the molecule Y–C_2 in H_2O, H_2CO and pyridine, C_3 in H_3N and C_∞ in HF; σ...plane of symmetry in Y containing the highest number of σ-bonds)

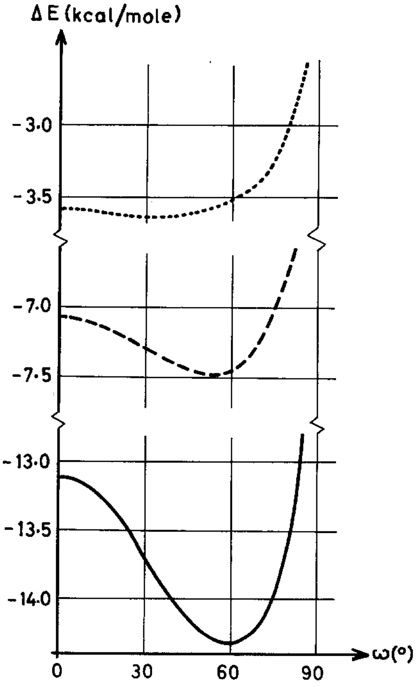


Fig. 2. Angular dependence of hydrogen bonds to the carbonyl group ($\vartheta = 0°$; ——— H_2CO/HF, – – – – H_2CO/HOH and ... H_2CO/HNH_2)

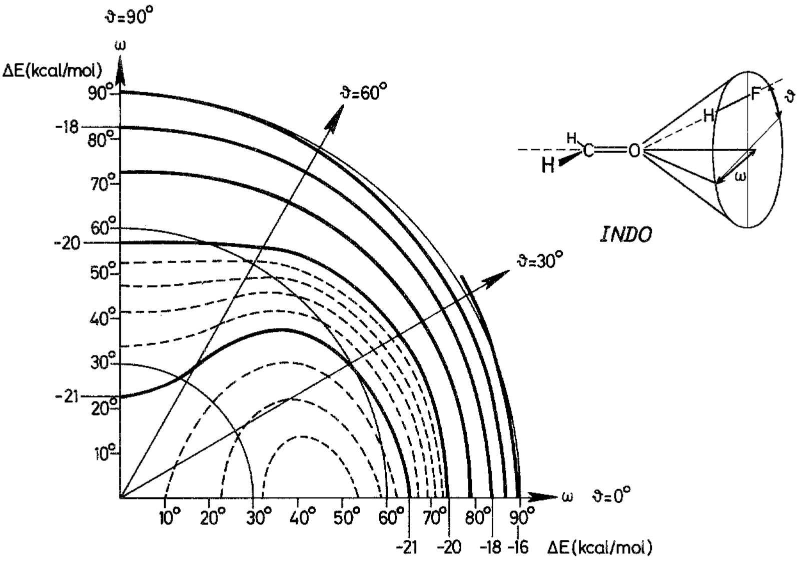


Fig. 3. Energy surface, $E(\omega, \vartheta)$ of H_2CO/HF ($R_{OF} = 2.36$ Å, INDO-calc.)

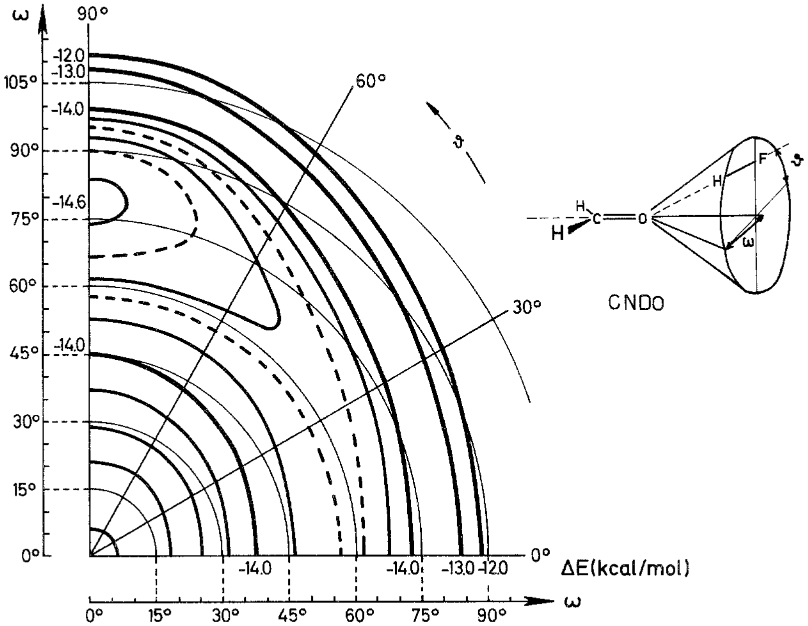


Fig. 4. Energy surface, $E(\omega, \vartheta)$ of H_2CO/HF ($R_{OF} = 2.44$ Å, CNDO/2-calc.)

the angular dependence can be described by a two dimensional energy surface $E(\omega, \vartheta)$. Additionally HF forms the strongest hydrogen bonds of our proton donors — HF, H_2O and H_3N — and hence we expect the largest influence of ω and ϑ on the energy in this case (Fig. 2). Finally in one example — form-

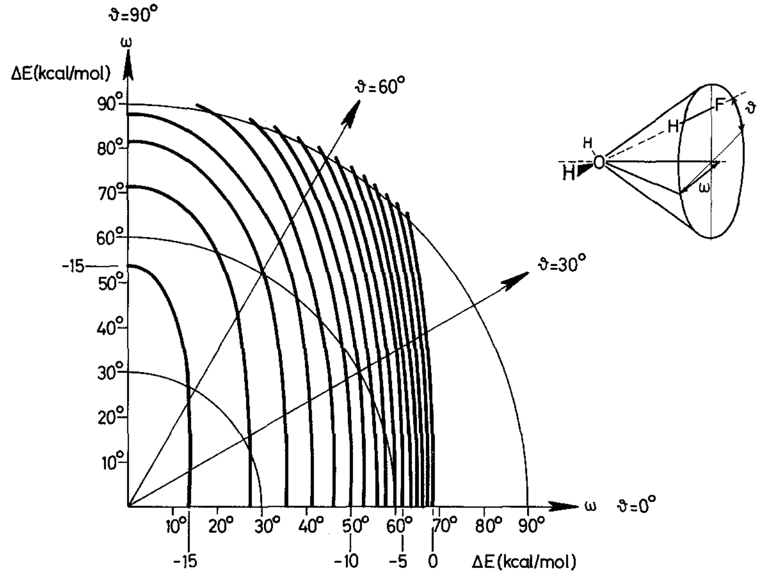


Fig. 5. Energy surface, $E(\omega, \vartheta)$ of H_2O/HF ($R_{OF} = 2.42$ Å, CNDO/2-calc.)

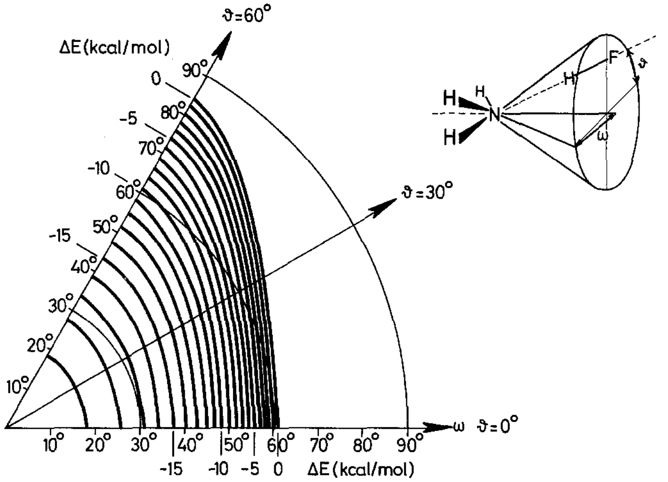


Fig. 6. Energy surface, $E(\omega, \vartheta)$ of H_3N/HF ($R_{NF} = 2.46$ Å, CNDO/2-calc.)

aldehyde/HF — we verified that ω and ϑ don't shift the energy minimum very much in the $\overline{XY}$ direction.

The influence of the one centre exchange integrals, which are neglected in the CNDO-procedure, on the results was tested in one example — formaldehyde/HF: We calculated the whole energy surface using the INDO-method (Fig. 3).

Typical examples of CNDO/2 energy surfaces, $E(\omega, \vartheta)$, are shown in Fig. 4 (H_2CO/HF), Fig. 5 (H_2O/HF) and Fig. 6 (H_3N/HF).

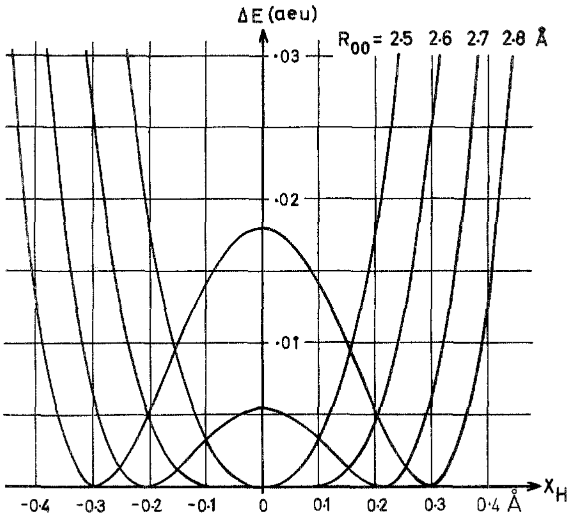


Fig. 7. Potential curves for protontransfer in $[H_2O...H...OH_2]^+$

In $(HF)_2$ the total energy is independent of ϑ because of the linearity of the monomers. A twisted arrangement ($\omega = 45°$) has the lowest energy. The energy surface of H_2CO/HF (Fig. 4) is of the same type. It shows a flat groove approximately following a cycle ($80° > \omega > 60°$; $0° < \vartheta < 360°$). All the other systems prefer the most symmetrical structure ($\omega = 0°$).

Energy curves describing the proton transfer from X to Y were calculated for two systems: $H_3N\cdots H{-}OH$ and $[H_2O\cdots H\cdots OH_2]^+$. Since the minimum energy geometries calculated by the CNDO/2 method differ from the experimental values, calculations were performed with a series of different distances of the two heavy atoms R_{XY} (Fig. 7).

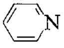
Discussion

1. Hydrogen Bond Energies and Charge Transfer

Looking at Table 2 more closely we find that the distance of the two heavy atoms, R_{XY}, is not correlated with the hydrogen bond strength in a simple manner. R_{XY} depends on both, the nature of the atoms and the strength of the hydrogen bond. However, the elongation of the HX bond, ΔR_{HX}, is much more appropriate for a comparison of hydrogen bonds between different atoms. In structures with weak hydrogen bonds the changes in the charge distributions and geometries of the two molecules have the character of small perturbations. The changes in strongly interacting systems are large: Comparison with weak hydrogen bonds indicate an increase in stabilization energies, changes in charge distribution and elongation of the HX bond by about one order of magnitude.

Changes in the potential curves of the HX streching vibration are recognized most easily as change of the force constants, which were calculated as curvatures at the energy minimum (Table 3). The absolute values of the force constants

Table 3. *HF stretching force constants in several hydrogen bonded structures* (Y···H–F)

Y	k [10^5 dyn/cm]	ΔE_{HB} (kcal/mole)
–	19.7[a]	–
HF	18.2	9.4
H_2O	17.0	15.4
	16.0	19.4
H_3N	16.0	20.0

[a] HF stretching force constant in the isolated molecule [15].

Table 4. *Comparison of calculated and experimental data*

	R_{YX} (Å) (calc)	R_{YX} (Å) (exp.)[a]	ΔE_{HB} (kcal/mole)	ΔH_{exp}[b] (kcal/mole)	Refs.
$H_3N\cdots HNH_2$	2.74	3.10	5.8	4.4	[20]
$H_2O\cdots HOH$	2.54	2.76	8.7	5.0	[20]
$HF\cdots HF$	2.44	2.49	9.4	6.8	[20]
$[H_2O\cdots H\cdots OH_2]$[a]	2.34	–	60	32	[18, 23]
$[HO\cdots H\cdots OH]^-$	2.34	–	72	35	[18, 23]
$[F\cdots H\cdots F]^-$	2.25	2.26	106	40—60	[21, 22]

[a] *X*-ray diffraction data [20].

[b] Enthalpies of dimerization in the vapour phase [20] or data derived from thermochemical cycles [21, 22] or threshold measurements [18, 23].

calculated from CNDO/2 energy curves are by far too large [15], but the decrease in the force constant with increasing hydrogen bond strength agrees well with the shift towards longer wave lengths known from IR-spectra of hydrogen bonded systems.

In Table 4 the calculated results are compared with the available experimental data. As reported previously in the formaldehyd/water case the minimum energy distance of the two heavy atoms, R_{XY}, is calculated somewhat too small. Accordingly the interaction energies are too large. In weakly hydrogen bonded structures the difference between the calculated energies and the reaction enthalpies in the vapour phase is about 30%. This difference increases with increasing hydrogen bond strength reaching about 100% in systems with strong hydrogen bonds.

The results of INDO-calculations on the system formaldehyde/HF are very similar to those of the CNDO/2-calculations. However, the agreement with experimental data is worse: The distance between the molecules (R_{XY}) is somewhat smaller, the interaction energy is larger than in CNDO/2-calculations. Hence in the field of hydrogen bonding the inclusion of one centre exchange integrals does not improve the results.

As reported previously [4] a small amount of electron charge is transfered along the hydrogen bond. The molecule, which carries the lone pair acts as electron donor. In weakly hydrogen bonded systems an interesting almost linear relationship is found between the amount of charge transfer (Δq) and the stabilization energy (Fig. 8). This result supports the idea of Bratoz [1],

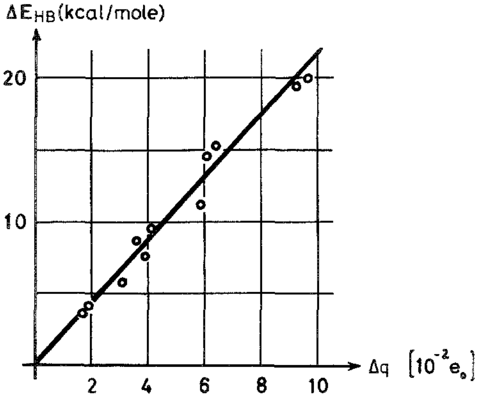


Fig. 8. Correlation between charge transfer (Δq) and interaction energy (ΔE_{HB}) in structures with weak hydrogen bonds

Puranik and Kumar [16], that the main stabilization of the hydrogen bond is due to charge transfer. As expected no such relation can be found in systems with strong hydrogen bonds, where the orbitals of the two molecules are mixed extensively and the amount of charge transfer is by no means small (Table 2).

2. *Stereochemistry of Hydrogen Bonds*

The calculations of relevant energy surfaces is a tricky problem, because the shape of flat hollows can be changed drastically by small differences in the basis set or in the method of calculation. Hence we calculated the most shallow energy surface with and without one centre exchange integrals. At first sight the surfaces describing angular dependence of hydrogen bonding in formaldehyde/HF calculated by the CNDO/2- and the INDO-method differ strongly (Fig. 4 and Fig. 3). The CNDO/2-calculations favour the interaction of the proton with the π-electrons of formaldehyd. The energy minimum if found at $\omega = 80°$, $\vartheta = 90°$ and 270°. The most stable arrangement of the INDO-calculations lies in the plane of the formaldehyd molecule — $\omega = 60°$, $\vartheta = 0°$ and 180°. However, both methods indicate that the completly linear arrangement, C, O, H and F on a straight line has not the lowest energy. Apart from the differences concerning the shape of the flat groove around the energy minimum both calculations — CNDO/2 and INDO — show that ω and ϑ have only slight influence on the total energy. Therefore some confidence can be attributed to the calculated results, if we do not look at too small energy differences.

In general the directive properties of hydrogen bonds increase with the hydrogen bond strength. Fig. 2 indicates a decrease of the potential barrier at $\omega = 0°$ in hydrogen bonding to carbonyl groups, when we proceed from HF to H_2O and H_3N. Hydrogen bonds between CO and NH groups most frequently occurring in peptides and proteins are extremely insensitive to angular deformation in the range $80° > \omega > 0°$.

The flexibility of hydrogen bonded systems can be described best in form of areas in the ω, ϑ-diagram, which cover all conformations lying up to one rsp. two

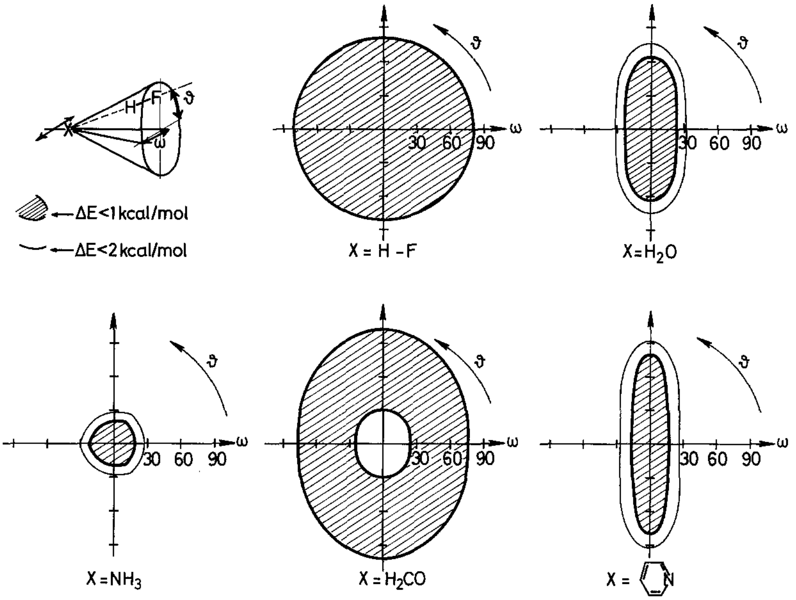


Fig. 9. Angular dependence of hydrogen bond energies in X/HF (the areas drawn cover all configurations up to 1 resp. 2 kcal/mole above the energy minimum)

kcal/mole above the energy minimum (Fig. 9). We can distinguish three different types of lone pair donors:

Formaldehyde and HF form almost equally stable hydrogen bonds in the range $\omega < 80°$ independent of the particular value of ϑ. Water and pyridine show flexibility for hydrogen bond in one plane ($\vartheta = 90°$, $270°$; $0 \leq \omega < 80°$); in the direction perpendicular to this plane the energy increases rapidly and the whole stabilization due to the hydrogen bond is lost soon. The last type of lone pair donors, ammonia, can form stable hydrogen bonds exclusively in one direction ($\omega = 0°$).

The results can easily be generalized: π-electrons and lone pairs are both involved in hydrogen bonding. The stereochemistry of the hydrogen bond is therefore determined by the number of σ-bonds ending in the acceptor atom: One σ-bond allows two dimensional flexibility for hydrogen bonding. Acceptor atoms with two σ-bonds are insensitive to deformations along a straight line. Hydrogen bonds to atoms with three σ-bonds are restricted to one direction.

3. *Hydrogen Bonds and Proton Transfer*

At first we regard two neutral moleculs — Y and HX, which form together a weak hydrogen bond. Proton tranfer from one molecule to the other is highly endothermic in the vapour phase, since it introduces charge separation (2):

$$\underset{\boldsymbol{A}}{\mathrm{Y} + \mathrm{HX}} \rightleftarrows \underset{\boldsymbol{B}}{[\mathrm{Y}-\mathrm{H}]^+ + \mathrm{X}^-}, \qquad (2)$$

$$\Delta E_{\mathrm{PT}} = E_{\mathrm{X}^-} + E_{\mathrm{YH}^+} - (E_{\mathrm{Y}} + E_{\mathrm{HX}}).$$

Table 5. *Comparison of calculated and experimental proton affinities*

Molecule or ion	CNDO/2	ΔE_{PA} (kcal/mole) *ab initio*[a] basis set minimum	largest applied	exp[a]
HF	-182	-401	-108	–
H_2O	-246	-345	-181	-151 (-181[b])
H_3N	-299	-303	-220	-206
$F^{\ominus}$	-598	-1022	-387	-361
$HO^{\ominus}$	-608	-785	-403	-370
$H_2N^{\ominus}$	-625	-627	-427	-380

[a] The values are taken from [17].
[b] Recent measurement [18].

In aqueous solution this large energy difference is of course dimimished drastically by the solvation energies of the ions.

CNDO/2 calculations on the proton transfer in the hydrogen bonded system $H_3N\cdots H\text{–}OH$ lead to unsymmetrical potential curves at distances, which are typical for structures with hydrogen bonds — $2.6 < R_{NO} < 3.2$ Å. The energy difference between the structures ***A*** and ***B*** is by far larger than the coulomb interaction of the two ions. Therefore the second energy minimum corresponding to

$$[Y\text{–}H]^+\cdots X^-$$

disappears in the steep slope of the curve.

The energies for proton transfer are composed of two proton affinities:

$$\begin{aligned} \Delta E_{PT} &= \Delta E_{PA}(Y) - \Delta E_{PA}(X^-)\,, \\ \Delta E_{PA}(Y) &= E_{[H-Y]^+} - (E_{H^+} + E_Y)\,. \end{aligned} \tag{3}$$

In order to find out, whether CNDO calculations on proton transfer are reliable or not, we compared the calculated proton affinities (ΔE_{PT}) with the available experimental data and the results of *ab initio* LCAO–MO–SCF calculations [17]. The CNDO/2-values are much better than those calculated with minimum basis sets (Table 5). However, when compared with the best *ab initio* calculations available or with experimental data, the CNDO results are rather poor. All proton affinities are too large. The CNDO method overemphasizes the stability of cations. In contrary the calculated energies for anions are by far too large. These errors are compensated to some extent, when proton tranfer energies are formed (3). However the CNDO values for ΔE_{PT} are still too large by about 50%. On the other hand it is encouraging that the relative values of CNDO calculations agree well with both *ab initio* and experimental data.

Although the CNDO values for proton transfer energies are too large, no double minimum potential can be expected for weak hydrogen bonds, since the correct ΔE_{PT} values are still very high.

Table 6. *Comparison of calculated and experimental energies for proton transfer reactions (2)*

Molecules	ΔE_{PT} (kcal/mole)			ΔE_{HB}
	exp	*ab initio*	CNDO/2	CNDO/2
$H_3N+H\text{-}F$	155	166	299	20.0
$H_3N+H\text{-}OH$	164	183	309	11.2
$H_3N+H\text{-}NH_2$	177	207	326	5.8
$H_2O+H\text{-}F$	210	205	351	15.4
$H_2O+H\text{-}OH$	219	222	361	8.7
$H_2O+H\text{-}NH_2$	229	246	378	4.5
$HF+H\text{-}F$	–	278	416	9.6

In Table 6 proton transfer energies are compared with the stabilization energies for hydrogen bonds. No general relationship can be found. For one particular base (Y) the strength of the hydrogen bond increases together with the acidity of the second molecule, HX (decreasing ΔE_{PT} value). For one particular acid an analogous relation holds, increasing hydrogen bond strength with increasing basicity of the partner molecule (decreasing ΔE_{PT} value). However, the basicity of the lone pair has much more influence on proton transfer energies than on hydrogen bonds. This result seems reasonable, since in all systems with weak hydrogen bonds R_{YH} is much larger than R_{HX}.

Proton transfer from a cation to a neutral molecule or from a neutral molecule to an anion does not seperate charges:

$$Y+HX^+ \rightleftarrows YH^+ + X\,,$$
$$Y^- + HX \rightleftarrows YH + X^-\,.$$

In these systems the energies of both structures with the proton left or right do not differ as much as before. If the structures are identical by symmetry, extremely stable hydrogen bonds are formed (Table 2).

In $[H_2O\cdots H\text{-}OH_2]^+$ the energy curves for the proton transfer show two minima at large OO distances — $R_{OO} > 2.6$ Å (Fig. 7). When the distance between the two oxygens is increased, the height of the barrier grows rapidly. Below $R_{OO} = 2.6$ Å a symmetrical single minimum potential is obtained. Calculations of the nuclear motion along these potential curves are now in progress. The calculated rates for proton exchange will show, whether the potential curves obtained by semiempirical LCAO–MO methods are reliable or not.

Conclusion

The CNDO method has been applied successfully to a variety of hydrogen bonds between small molecules and ions. An uniform treatment of weak and strong hydrogen bonds is possible. As far as experimental data are available the relative order of bond strength is predicted correctly.

π-electrons and lone pairs seem to be equally well suited as acceptors for hydrogen bonds. As long as the three atoms Y, H and X lie on a straight line, the stereochemistry of hydrogen bonds is largely determined by the interaction of the non bonded parts of the molecules. In the case of small proton donor molecules the flexibility of the hydrogen bonded structure is limited more and more by an increasing number of σ-bonds to the acceptor atom Y.

The values of proton affinities obtained by CNDO calculations or by *ab initio* calculations with small basis sets are much too high. The absolute values of proton transfer energies are too high as well, but the relative order is predicted correctly by CNDO calculations. In general these errors limit the reliability of potential curves for proton transfer seriously. However, no error of this type is introduced in the calculations of symmetrical hydrogen bonds, where both structures with the proton on the right and on the left have the same energy.

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