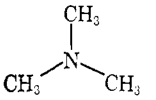
Table VIII. Energy Levels of Diazabicyclic Compounds

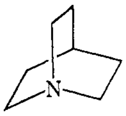
Molecule	XII (D_{3h})	XIII (C_{2v})	XIV (C_{2v})	XV (D_{3h})
E(LUMO)	-3.257 e'	-3.269 b_2	-4.259 a_2	-5.175 e''
E(HOMO)	-11.849 a_1'S	-12.618 a_1S	-12.519 b_1A	-11.885 a_2''A
E (other lone pair combination)	-13.422 a_2''A	-12.989 b_1A	-13.124 a_1S	-14.763 a_1'S

This can be interpreted as follows. Each two-carbon bridge is in the most favorable orientation for through-bond coupling of the two lone paris. This coupling puts A below S. As one-carbon bridges are substituted for two-carbon bridges the through-bond coupling becomes inefficient while the through-space coupling increases since the bridgeheads come closer together. This direct coupling always puts S below A.

To provide some models in which lone-pair interaction is lacking we have calculated trimethylamine (XVI) and quinuclidine (XVII). The lone-pair orbitals are at -12.754 in XVI and -12.261 eV in XVII.



XVI



XVII

We have not been able to find any reports of the molecules XIII, XIV, and XV in the literature.[25] Our calculations predict a red shift in the n → σ^* transition in XII and XV but less for XIII and XIV. It seems to us that the synthesis of XIII should be feasible; the molecule would be of considerable theoretical interest.

Acknowledgment. We are grateful to H. E. Simmons for some stimulating discussions. The Quantum Chemistry Program Exchange kindly provided the POLYATOM program authored by I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, S. Seung, B. T. Sutcliffe, and M. P. Barnett. This work has been supported in part by the National Science Foundation, the National Institutes of Health, and the Chevron and Sloan Foundations.

[25] A diquaternary salt of XIII is known: G. R. Pettit and J. A. Settepani, *Chem. Ind.* (London), 1805 (1964).

Hydrogen Bonding in Pyridine[1]

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Abstract: The pyridine–water and pyridine–methanol hydrogen-bonded systems have been examined using the extended Hückel theory (EHT). Of the various conformations studied, the one in which the hydrogen approaches the pyridine lone pair forming a linear arrangement of the O–H···N grouping is of lowest energy. In this case, for both water and methanol, a reasonable potential energy curve is obtained for the hydrogen-bonded system. From this curve it is concluded that the heat of formation is -2.3 kcal/mol, the equilibrium distance between the oxygen and nitrogen atom 2.76 A, and the force constant $0.10–0.11 \times 10^5$ dyn/cm. The nitrogen lone-pair orbital shifts progressively to lower energy as water or methanol approachs the pyridine molecule. The calculated blue shift is about twice as large for water than methanol. At fixed positions of the heavy nuclei, the proton was transferred from oxygen to the nitrogen atom. A double energy minimum was obtained with an energy barrier of approximately 0.7 eV for the proton transfer at the equilibrium distance of O–N separation. As the proton shifts over from oxygen to nitrogen, as expected, the O–H overlap population decreases and the H–N increases. While the charge on oxygen increases and for nitrogen decreases, it stays essentially constant at about +0.4 electron for hydrogen during the transfer. For the (n,π^*) excited state, the results parallel qualitatively those for the ground state. Finally, it is of interest to mention that the carbon-13 chemical shifts, calculated from the EHT wave function, are in reasonable agreement with the experimental values.

A great number of facts about the hydrogen bond are fairly well understood; what is not so clear is the interpretation that should be given to them. Pimentel and McClellan,[3] Coulson,[4] and Bratoz[5] provided reviews of the concepts used in the theoretical interpretation of the hydrogen bond. These will be presented in brief form before discussing our calculations.

The classical electrostatic model of the hydrogen bond has enjoyed substantial support and there are two main

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[1] This work was supported by a research grant from the University of Puerto Rico. It was presented at the Euchem Symposium held on April 16–21, 1967, in Mittenwald, Germany.

[2] Cornell University, Ithaca, N. Y.

[3] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Chapter 8.

[4] C. A. Coulson in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959.

[5] S. Bratoz in "Advances in Quantum Chemistry," Vol. III, P. O. Löwdin, Ed., Academic Press Inc., New York, N. Y., 1967.

reasons for this. First, according to Pauling,[6] the hydrogen bond must be ionic in nature since the bonding properties of the hydrogen atom depend on the 1s orbital. For this reason, hydrogen is univalent forming only one covalent bond. Second, this model offers the opportunity of quantitative calculations of hydrogen-bond behavior. For example, when calculating the heat of formation of the O–H···O system by the simplest electrostatic point-charge model, the results are quite satisfactory, but they depend critically on the choice of the point charges and their positions. When more realistic charge distributions are used, the results differ little from those obtained with the simple electrostatic model. In order to obtain reasonable heats of formation of the hydrogen-bonded systems, the heavy nuclei have to be placed at a distance of separation less than the sum of the respective van der Waals radii. This seems to indicate that in addition repulsive forces other than electrostatic forces are operative. On the other hand, the valence-bond treatment attempts to determine the amount of covalent contribution to the hydrogen bond. This contribution is found to be quite important, but sometimes the values of the coefficients of the possible valence-bond structures provide no reassurance of the validity of such calculations. However, valence-bond descriptions explain some properties, such as certain features of infrared and nuclear magnetic resonance spectra,[7] not readily handled by the electrostatic model.

The alternative molecular orbital description has not received proper attention until recently. Several papers have been published, among them one by Pimentel,[8] another by Nagakura,[9] some by Mataga,[10–12] and a series by Fukui and coworkers.[13–15] A recent critical survey of MO theories of hydrogen bonding has been presented by Bratoz.[5] Pimentel considered HF_2^-, using only fluorine 2p orbitals, directed along the bond, and the hydrogen 1s orbital. His results show that the molecular orbital theory provides a qualitative basis for understanding the hydrogen bond. Fukui and coworkers studied inter- and intramolecular hydrogen bonding by using the extended Hückel theory, developed by Hoffmann,[16] and another simple LCAO MO method for σ-electron systems.[17] In these methods the whole molecule with all its valence electrons is considered and not an unreal fragment of it.

The observed parallelism between experiment and theory has encouraged us to examine other hydrogen-bonding systems using the EHT method. Guided by our interest in heterocyclic molecules, we decided to study the pyridine–water and pyridine–methanol system. Our initial interest in these cases was to see the effect on the nitrogen lone pair of pyridine as the water or methanol molecules are allowed to approach.

Details of the Calculation

In the extended Hückel theory[16] the basis set for the linear combination of atomic orbitals $\psi_i = \Sigma c_{ir}\phi_r$ is extended to include all valence shell atomic orbitals. Thus in the case of pyridine, the 1s Slater orbital for hydrogen and the 2s and three 2p Slater orbitals for carbon and nitrogen are used. Minimization of the total energy, in the Hückel approximation of the total Hamiltonian as a sum of one-electron effective Hamiltonians, gives the secular determinant

$$\det(H_{ij} - ES_{ij}) = 0$$

where i, j, go from 1 to n, *i.e.*, through the total number of atomic orbitals. All overlap integrals S_{ij} are retained and calculated from standard sources.[18] The exchange integrals H_{ij} are computed according to the approximation

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$$

where $K = 1.75$. The Coulomb integrals are taken as the valence-state ionization potentials. A Mulliken population analysis[19] finally yields the σ- and π-electron densities and overlap populations. A program for carrying out these calculations on the IBM 7094 computer has been described.[20]

The geometry of pyridine was approximated as an ideal hexagon. All ring bond lengths were taken as 1.40 Å and all carbon–hydrogen bond lengths as 1.10 Å. The water molecule was assumed to be tetrahedral with oxygen–hydrogen bond lengths of 0.96 Å. In methanol both the carbon and the oxygen atoms were regarded as tetrahedral centers with a carbon–oxygen bond length of 1.40 Å. The following values of the valence-state ionization potentials were used: H(1s) = −13.6 eV, C(2s) = −21.4 eV, C(2p) = −11.4 eV, N(2s) = −26.0 eV, N(2p) = −13.4 eV, O(2s) = −32.3 eV, and O(2p) = −14.8 eV. The Slater orbital exponents were taken as H, 1.30; C, 1.625; N, 1.950; and O, 2.275.

In one set of calculations, the hydrogen donor molecules, water and methanol, were allowed to approach the nitrogen lone pair of pyridine without altering the initially chosen geometries of the molecules. The computer input consisted of the atomic coordinates of the various atoms of the molecules involved. A number of configurations were considered which are shown in Figure 1. In the case of the water–pyridine system, the configurations **1–4** were chosen. In configuration **1**, the water molecule approaches the nitrogen lone pair in such a way that the hydrogen-bonded system O–H···N is a linear arrangement along the y axis. In other words, the proton moves head-on toward the nitrogen lone pair. The H···N distance was varied from 3.0 to 1.0 Å in steps of 0.5 Å. At each distance of separation, the water molecule was rotated around the axis of approach (the y axis) in steps of 15° from 0 to 90° in order to find the preferred orientation of the second hydrogen atom. In configuration **2**, the two hydrogen atoms bisect the nitrogen lone pair, while in

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[6] L. Pauling, *Proc. Nat. Acad. Sci. U. S.*, **14**, 359 (1928).

[7] H. Saito, K. Nukada, H. Kato, T. Yonezawa, and K. Fukui, *Tetrahedron Letters*, 111 (1965).

[8] G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

[9] S. Nagakura, *J. Chim. Phys.*, **61**, 217 (1964).

[10] S. Mataga and N. Mataga, *Z. Physik. Chem.* (Frankfurt), **19**, 231 (1959).

[11] N. Mataga and S. Tsuno, *Naturwissenschaften*, **45**, 333 (1958).

[12] S. Mataga and N. Mataga, *Bull. Chem. Soc. Jap.*, **32**, 511 (1959).

[13] K. Morokuma, H. Kato, T. Yonezawa, and K. Fukui, *ibid.*, **38**, 1263 (1965).

[14] H. Saito, T. Yonezawa, S. Matsuoka, and K. Fukui, *ibid.*, **39**, 989 (1966).

[15] T. Yonezawa, H. Saito, S. Matsuoka, and K. Fukui, *ibid.*, **38**, 1431 (1965).

[16] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[17] K. Fukui, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **33**, 1201 (1960).

[18] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[19] R. S. Mulliken, *ibid.*, **23**, 1833, 2338, 2343 (1955).

[20] R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).

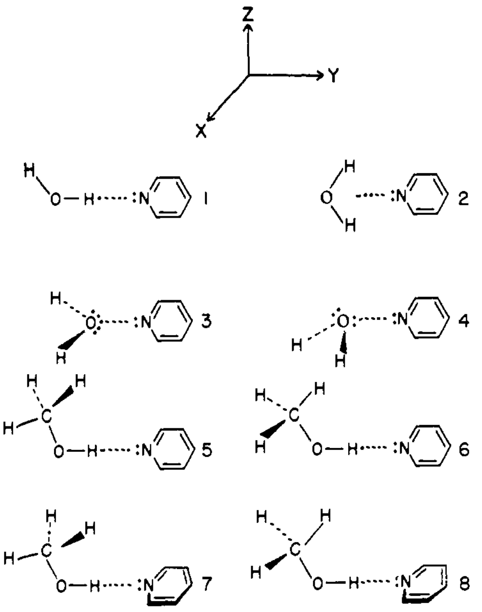


Figure 1. Configurations chosen for the pyridine-water and pyridine-methanol systems.

configuration **3**, the two oxygen lone pairs bisect the nitrogen lone pair. Finally, in configuration **4**, one of the oxygen lone pairs is in direct line of approach of the nitrogen lone pair along the y axis. The N-O-H angle projected on the yz plane is 125° here.

In the methanol-pyridine pair, the degrees of freedom are considerably greater. For practical reasons, configurations **5**-**8** were chosen. Again, the methanol molecule was allowed to approach the pyridine molecule as shown in the four configurations varying the H···N distance from 3.0 to 1.0 Å.

In another set of calculations of the water-pyridine system, the oxygen and nitrogen atoms were kept at a fixed distance of separation, but the proton was allowed to be transferred from an initial distance of 0.5 Å away from the oxygen atom to a final distance of 0.5 Å away from the nitrogen in steps of 0.1 Å. For each case the ground state and the first excited configuration (n,π^*) was calculated. The highest occupied σ orbital, while considerably delocalized, is still identifiable with the spectroscopic N lone pair, and is designated as n.

Results and Discussions

Of the four configurations that were considered for the water-pyridine pair, only configuration **1** leads to an energy minimum as the water molecule moves toward the nitrogen lone pair. This energy minimum is shown in Figure 2, where the total energy of the water-pyridine system is plotted against H···N separation. A similar curve is obtained for the (n,π^*) excited state. The orientation of the second hydrogen atom is irrelevant since the energy differences are minute as the water molecule is rotated about the axis of approach, the y axis. For this reason, all of the following discussion will be restricted to that arrangement in which the water and pyridine molecules lie in the same plane. For comparison, the energy variation as a function of distance of separation is shown in Figure 3 for the four conformations of the water-pyridine pair. Due to the large energy differences between these configurations, the energy minimum for configuration **1** is hardly noticeable. However, it is immediately apparent from this figure that the hydrogen bond prefers a linear geometry of the bonded atoms O-H···N. For example, in configuration **2**, in which the two hydrogen atoms bisect the lone pair, the possibility exists of both hydrogens overlapping with the nitrogen lone pair. On the contrary, of the configurations considered, this configuration is of highest energy and clearly shows no energy minimum. That these calculations reveal in a reasonable way the hydrogen-bonding phenomenon is brought out in configurations **3** and **4**. Here the oxygen lone pairs approach the nitrogen lone pair and, as expected, on decreasing H···N separation, the total energy of the system increases.

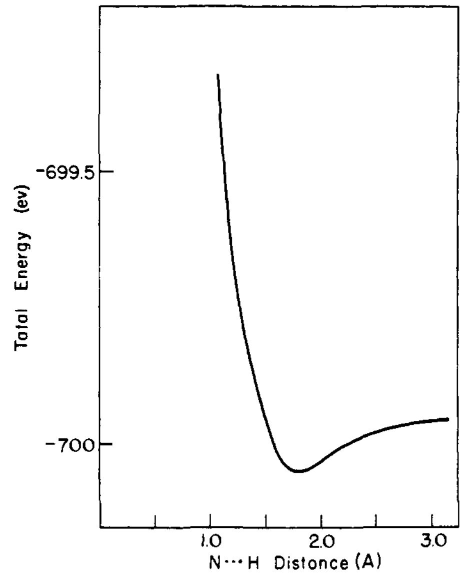


Figure 2. Total energy of configuration **1** of the water-pyridine pair as a function of N···H distance.

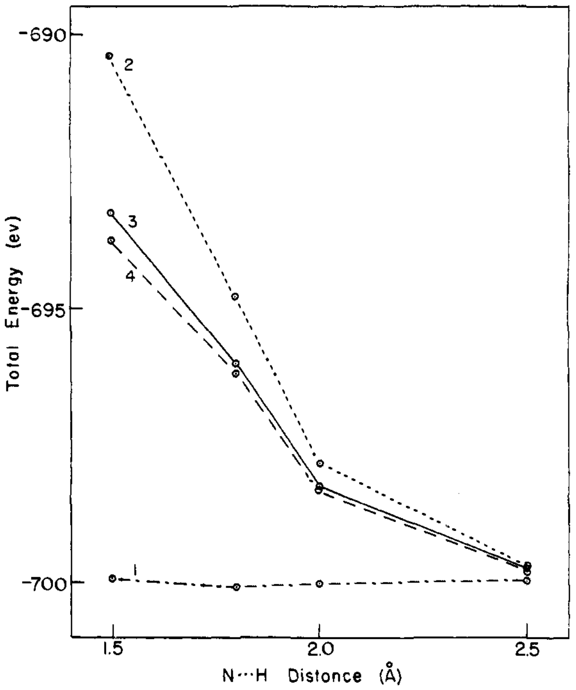


Figure 3. Potential energy curves of the pyridine-water configurations.

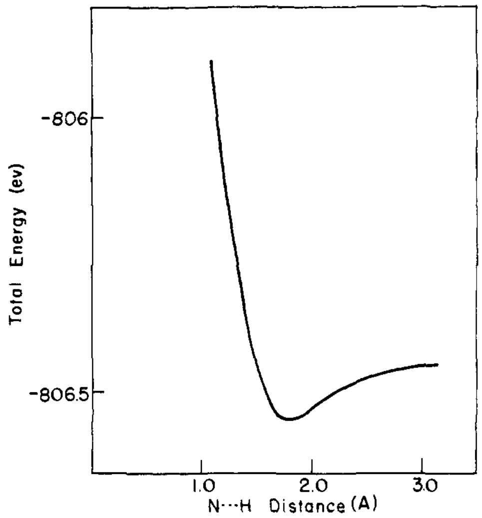


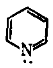
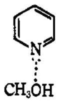
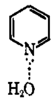
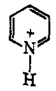
Figure 4. Total energy of configuration 7 of the methanol–pyridine pair as a function of N$\cdots$H distance.

One word of caution concerning these calculations is worthwhile of mention. No efforts have been made to minimize the geometry of the approaching water molecule. Quite arbitrarily we have chosen a static tetrahedral geometry of the approaching water molecule, while in fact the geometry of minimum energy for water according to EHT calculations is linear. We feel that the qualitative aspects of the potential energy curve should remain essentially the same. What is important here is that the O–H bond comes in linearly toward the nitrogen lone pair along the y axis. As pointed out before, the orientation of the second proton is quite irrelevant. A more detailed study would require that the geometry of the water molecule be changed as it moves toward pyridine. For that matter, the pyridine geometry should also be changed since it goes over to a pyridinium ion. However, owing to the large number of degrees of freedom of the system, the little additional information gained from such a study hardly justifies the effort as well as computer time.

The results for the methanol–pyridine system parallel those of the water–pyridine pair. In view of the conclusions for the water–pyridine system, in all four methanol configurations, the O–H$\cdots$N grouping is taken to be linear. The only difference arises in the orientation of the methyl group. Either the carbon atom of the methyl group is in the plane of the pyridine ring, configurations **5** and **6**, or perpendicular like in **7** and **8** (Figure 1). Further distinctions are made concerning the orientation of the methyl hydrogens. In all four configurations of the methyl group an energy minimum is obtained, as evidenced in Figure 4. Of the four configurations, **7** is of lowest energy and **6** of highest energy. Even then, the difference in energy is only about 0.5 kcal/mol. We shall only make reference to configuration **7** of the methanol–pyridine pair, the most stable arrangement.

It is now of interest to consider the fate of the lone-pair orbital as the hydrogen donor, water or methanol, approaches the pyridine molecule. As the overlap between the 1s orbital of hydrogen and the nitrogen lone pair increases, it is expected that the lone-pair orbital progressively becomes more bonding and thus shifts to lower energy. Finally, as the pyridinium ion is formed, the lone-pair orbital has been completely converted into a H–N σ bond. The results are summarized in Table I. The lone pair energy for water–pyridine and methanol–pyridine are quoted for the equilibrium distance of separation of the molecules. The expected effect is evident.

Table I. Lone-Pair Energies (eV) of the Various Hydrogen-Bonded Systems; the Energy of the Highest Occupied Orbital Is Listed

Molecule	E, eV	Orbital type
	−12.618	n
	−12.635	n
	−12.640	n
	−13.590	σ

In Table II are summarized the total charges and overlap populations of the hydrogen-bonded systems. For comparison, the pyridine molecule and the pyridinium ion are included. The values of the pyridine–methanol and pyridine–water system are quoted for the most stable configurations, respectively **7** and **1**, at their equilibrium distance of separation. As expected, the negative charge on nitrogen decreases as we go from pyridine to the pyridinium ion because progressively the lone-pair orbital is converted to an N–H σ bond. Of particular interest is that the total charge on the C_α atom becomes less positive as we go from pyridine to the pyridinium ion. This implies that on protonation the electron density at C_α increases. Although this is contrary to chemical intuition, carbon-13 chemical shifts support this idea.[21] The charge distribution for the lowest (n,π^*) excited state of the water–pyridine system suggests that the excess negative charge on nitrogen is forced into the C_α and C_β positions. Comparing the overlap populations in this table, it is clearly indicated that a weak H–N bond is formed between water and pyridine, as well as methanol and pyridine. Finally, from the overlap population of the (n,π^*) excited state of the pyridine–water pair, it is concluded that the N–H bond is weaker in the excited state compared to the ground state.

After the O–H$\cdots$N equilibrium distance for the water–pyridine system was established, another series of calculations was performed where the O–H distance was varied while keeping the N$\cdots$O distance fixed at 3.01 Å, 2.76 Å (equilibrium distance), and 2.51 Å. The results are exhibited in Figure 5, where the total energy of the system is plotted *vs.* the position of the hydrogen atom. The motion of the proton in this hy-

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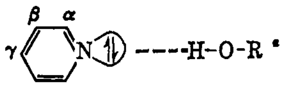
[21] (a) R. J. Pugmire, Ph.D. Thesis, University of Utah, June 1966. (b) A. Mathias and V. M. S. Gil, *Tetrahedron Letters*, 3163 (1965).

Table II. Total Charges and Overlap Populations of the Various Hydrogen-Bonded Pyridine Systems for the Molecules at Their Equilibrium Distance of Separation



System	Total charges N	C_α	C_β	C_γ	Overlap populations H	O-H	H···N
Pyridine	−0.891	+0.369	−0.046	+0.110	...	...	...
Pyridine-methanol	−0.825	+0.366	−0.046	+0.110	+0.434	0.5472	0.0723
Pyridine-water (gs)[b]	−0.825	+0.366	−0.046	+0.110	+0.427	0.5437	0.0720
(n,π*)	−0.574	+0.239	−0.028	−0.173	+0.430	0.5527	0.0595
Pyridinium ion	−0.073	+0.338	−0.038	+0.109	+0.214	...	0.6710

[a] Where R = H or CH_3. [b] Ground state.

drogen bond is described by a double potential minimum in which the proton may assume two stable positions, one near the oxygen and the other near the nitrogen atom. The energy barrier toward proton transfer from oxygen to nitrogen for the equilibrium configuration of 2.76 Å amounts to approximately 15 kcal/mol. Furthermore, the N-H energy minimum is by 50 kcal/mol lower in energy than the O-H energy well. The proton affinity for nitrogen is greater than for oxygen. For example, comparing the p*K* of pyridine and water, which are respectively 5.2 and 4.0, the N-H minimum is expected to be deeper. However, the complicating feature here is the fact that at the O-H minimum the structure of the hydrogen-bonded system is O-H···N with little charge separation. On the other hand, at the N-H minimum we have the fully charged structure O^-···N-H^+. On the basis of simple electrostatic considerations, it is clear that the O-H···N structure should be more stable than the polar O^-···H-N^+ structure. For this reason it would be expected that the O-H minimum should be of lower energy compared to the H-N minimum. The discrepancy here is of course due to the lack of electron correlation in the Hückel method[13] which results in exaggerated charge separation. As a consequence, our EHT calculations place the charged structure at lower energy relative to the neutral one. A related deficiency of these calculations is evident from Figure 5, that the energy minima are too close to the oxygen and nitrogen atom, respectively 0.60 and 0.65 Å. The O-H and H-N minima should lie at about 0.96 and 1.0 Å, respectively. In view of these complications, the details of the energy barrier for proton transfer are questionable. Quite generally it has been recognized that the energy barrier for the proton motion in a hydrogen bond varies substantially with the choice of the theoretical model.[22] The fact that the EHT does reproduce a double energy minimum is, however, most encouraging. We plan to repeat these calculations using a self-consistent field all-valence orbital method, namely Pople's CNDO method,[23] in order to obtain a more accurate picture of the proton motion in the O-H···N hydrogen bond of the pyridine-water pair.

The overlap populations for the O-H and N-H bonds, as the proton shifts from the oxygen to the nitrogen atom, are shown in Figure 6. As expected, the O-H bond population decreases while the H-N bond population increases as the proton approaches the nitrogen lone pair. At the equilibrium distance of the proton, about 1.0 Å away from the oxygen atom, the H-N population is approximately one-sixth of the O-H population. This again illustrates the weakness of the association. In Figure 7 are shown the net charges of the oxygen, nitrogen, and hydrogen atom for the O-H···N hydrogen bond in the water-pyridine pair. As the proton approaches the nitrogen lone pair, a large negative charge develops on oxygen, while a corresponding decrease of the negative charge on nitrogen is observed. Clearly the dipolar structure O^-···H-N^+ is formed. Of interest is the relative constancy of the positive charge on the hydrogen atom during this transfer. It varies from +0.45 near oxygen to about +0.30 near the nitrogen atom. These calculations were also carried out for the first excited state (n,π*). The results are quite similar to those obtained for the ground state of the water-pyridine pair. The energy barrier toward proton transfer is slightly higher, about 19.0 kcal/mol, and the difference

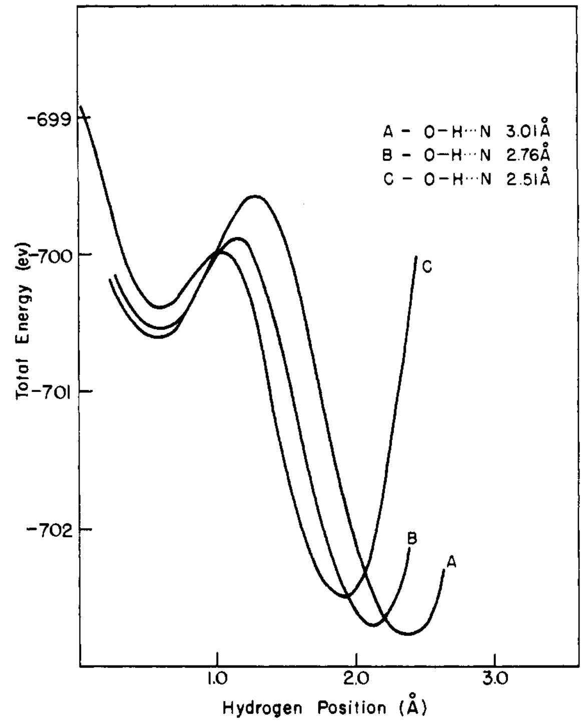


Figure 5. Total energy of configuration **1** of the water-pyridine system as a function of the position of the hydrogen atom.

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(22) R. Rein and F. E. Harris, *J. Chem. Phys.*, **41**, 3393 (1964).

(23) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S 129 (1965).

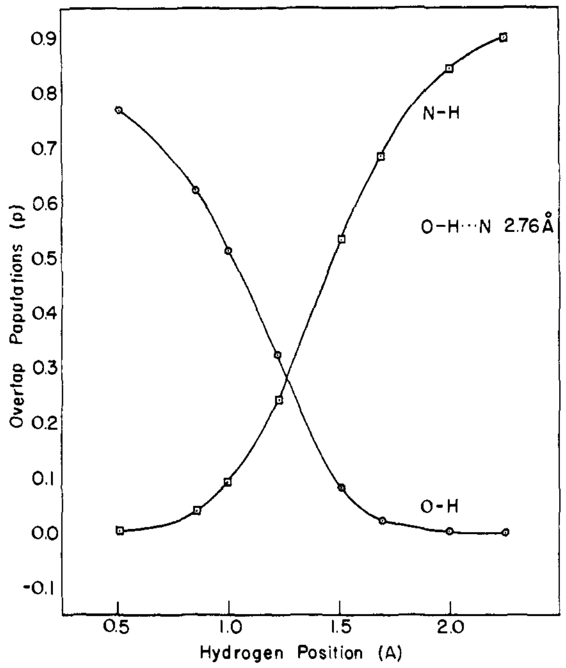

Figure 6. Overlap population of configuration **1** of the water-pyridine system as a function of the position of the hydrogen atom.

in the energy of the two minima slightly less, about 45.0 kcal/mol in favor of the H–N minimum. However, in view of the complications mentioned for the ground-state double potential minimum, the results for the excited state are even more questionable.

Unfortunately, no theoretical work is available on the hydrogen-bonded systems reported in this study. Consequently, the results of our calculations cannot be compared at this moment with more elaborate or sophisticated theories. It is clear, however, that the general conclusions drawn from the EHT calculations speak in favor of hydrogen bonding in pyridine using hydrogen donors like methanol and water. In the following section we shall examine, on the basis of our calculations, a number of specific properties which are usually considered as evidence for hydrogen bonding. For the sake of convenience, the properties are divided up into nonspectroscopic and spectroscopic properties.

A. Nonspectroscopic Properties. 1. Bond Length. For configurations **1** and **7** of the pyridine–water and pyridine–methanol pairs, respectively, the equilibrium $N\cdots H$ distance is found to be 1.8 Å. Since the O–H distance was taken as 0.96 Å, this makes the $O\text{–}H\cdots N$ bond length of the hydrogen-bonded system 2.76 Å. Experimentally it is found that for all O–H types of hydrogen bonds, the average $O\text{–}H\cdots N$ distance is 2.80 Å, the standard deviation being 0.09 Å.[24] This is in excellent agreement with the experimental results and indicates that the extended Hückel theory reproduces quite nicely the equilibrium bond distances in weakly bonded systems like the intermolecular hydrogen bond.

2. Enthalpy of Formation. From the depth of the energy minima in Figure 2 for the water–pyridine system and Figure 4 for the methanol–pyridine pair, the enthalpy of formation of the hydrogen bond may be estimated. In both cases we obtain a stabilization of approximately -2.3 kcal/mol. This value is close to the observed one for the methanol–pyridine pair of 3–4 kcal/mol.[25] It is a satisfactory estimate of the hydrogen-bond energy. The heat of formation calculated for the (n,π^*) excited state of water and pyridine is -1.5 kcal/mol compared to -2.3 kcal/mol for the ground state. This indicates, as already concluded from the corresponding overlap populations, that the hydrogen bond is weaker in the excited state. This is in agreement with experimental results which conclude that the hydrogen bond is weaker for the excited state relative to the ground state in nitrogen heterocyclics.[26]

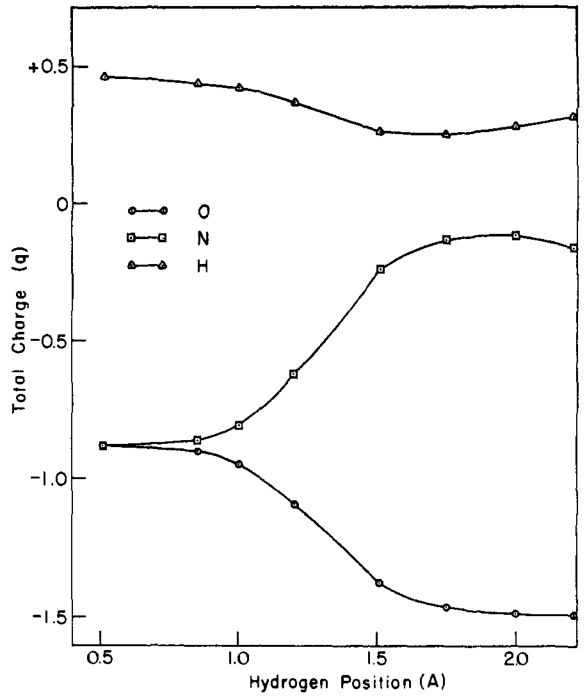

Figure 7. Total charges of the oxygen, nitrogen, and hydrogen atoms of configuration **1** of the water–pyridine system as a function of the position of the hydrogen atom.

3. Dipole Moments. Using the point-charge distributions of Table II and atomic coordinates, dipole moments were computed for pyridine, pyridine–water, and pyridine–methanol systems. In all three instances the value was found to be 4.72 D. First of all, this value is too high compared with the experimentally observed value of 2.25 D for pyridine itself.[27] This is of course due to the exaggerated charge separation observed in EHT calculations as well as using the point-charge model for calculating dipole moments rather than computing them as expectation values from the EHT wave functions directly. Secondly, our calculations suggest that the pyridine dipole moment is not altered by hydrogen bonding. Some change in the calculated dipole moments was expected, however, since the experimental dipole moment of pyridine in carbon tetrachloride and benzene solutions differs by 0.12 D.[28] Experimental studies of molecular polarizations of pyridine in water or methanol have not been carried out to our knowledge.

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B. Spectroscopic Properties. 1. Electronic Spectra. As shown in Table I, the nitrogen lone pair becomes progressively more bonding as we go from pyridine to the pyridinium ion. In the latter, a full H–N σ bond has been formed. Furthermore, the calculated energy level sequence of the lone pair, the π and σ orbitals, agree with the expected experimental order which is $\sigma < n < \pi^*$.[29] A theoretical treatment of hydrogen bonding and protonation effects on the electronic spectra of pyridine has been done by Mataga and Mataga.[10] They only considered the π electrons using Hartree–Fock SCF MO's for the pyridine–proton system. In our work we specifically investigated the $n \rightarrow \pi^*$ transition and corroborated Brealey and Kasha's proposition that the formation of the hydrogen bond lowers the energy of the lone-pair orbital.[30] From the energy level diagram it was concluded that the $n \rightarrow \pi^*$ transition energy of pyridine is about 25,365 cm^{-1}. This is considerably lower than the observed value of 34,769 cm^{-1} [31] for the vapor state of pyridine and points to a previously recognized deficiency of the EHT method.[32] Hückel-type calculations do not result in reasonable transition energies.

The calculated blue shifts for the $n \rightarrow \pi^*$ transitions correspond qualitatively to the experimental findings. The effect of solvents in other nitrogen heterocyclics is such that the shift in water is about twice as large as in methanol.[33] Since in our calculations the energy of the π^* level is virtually unchanged by the approach of water or methanol, from Table I one calculates blue shifts of 186 and 138 cm^{-1} for the pyridine–water and pyridine–methanol systems, respectively. These shifts have not been measured in pyridine because the $n \rightarrow \pi^*$ band disappears even when only small quantities of proton donors are added.[34,35] A shift of about 2000 cm^{-1} is expected to cause this effect.[34] In pyrazine the shifts are 700 and 1800 cm^{-1} for methanol and water solvents, respectively, while for pyridazine they are 2440 and 4000 cm^{-1}, respectively.[36] Our results for the blue shifts are too low compared with the experimental results, but qualitatively they are in the correct order. However, the red shift of the p band ($\pi \rightarrow \pi^*$ transition) is not reproduced by our calculations.[10,37]

2. Vibrational Spectra. As already pointed out from the overlap populations of Table II, a weak bond is formed between pyridine and the hydrogen donor. Fitting a quadratic to the potential energy minima of Figure 2 and Figure 4 in the region of 1.7 to 1.9 Å, we obtain the force constants of 0.11×10^5 dyn/cm for pyridine–methanol and 0.10×10^5 dyn/cm for pyridine–water.

The stretching force constants for the H$\cdots$N bond were also calculated using Scrocco's equation

$$k = \left[\frac{D_E}{S(1+S)^2}\left(\frac{\partial S}{\partial R}\right)^2\right]_{R_E}$$

where k is the force constant, D_E the dissociation energy, and S the overlap integral.[38] In our calculations the values of the overlap integrals between the nitrogen atom of pyridine and the hydrogen atom of the hydroxyl group in methanol and water were found to be equal. These overlap integrals were plotted as a function of distance and the partial derivative was evaluated at intervals of 0.01 and 0.02 Å. In both cases the partial derivative was equal to 0.5/Å. Using these values and assuming that the enthalpy of formation of the bonded molecules is equal to the dissociation energy of the hydrogen bond, the stretching force constant of the N$\cdots$H bond was calculated as 0.01×10^5 dyn/cm. This is one-tenth of the value determined by simple fitting of the quadratic. The A–H$\cdots$B vibrational mode is difficult to study because of its low frequency, about 50–250 cm^{-1}, and few experimental data are available. However, the value of 0.1×10^5 dyn/cm, determined from fitting a quadratic to the potential energy curve, agrees reasonably with the observed value for the pyridine–phenol complex which is 0.23×10^5 dyn/cm.[39] The results obtained from Scrocco's method are in poorer agreement with observed values.

The shape of the potential energy curves is another interesting feature. As shown in Figure 2 and Figure 4, these curves are strongly anharmonic. This fact is in agreement with Gross's explanation of the Raman spectrum of the formic acid crystal in the 255–170-cm^{-1} region.[40] The latter spectrum was interpreted on the basis of a very strongly anharmonic potential curve of the hydrogen bond. A theoretical scheme of the Raman spectrum was derived and the observed spectrum was found to be in accordance with the theory. Furthermore, the anharmonicity in the hydrogen bond is the topic of a series of papers by Sandorfy and coworkers.[41] They conclude that hydrogen bonding has a profound effect on the anharmonicity of O–H vibrations. This is opposite to what Pimentel and McClellan conclude in their book. Sandorfy's results lend support to the potential functions like ours which imply a large degree of anharmonicity.

The overlap population of the O–H bond decreases with hydrogen-bond formation. This corresponds qualitatively to the lowering of the O–H stretching frequency in the infrared spectrum.[1] The vibrational frequency changes in pyridine have been studied in several hydrogen donor solvents like water and methanol. Experimentally it has been observed that the skeletal vibrations of pyridine shift to higher frequencies.[42] From this it was concluded that the electron distribution in pyridine changes as a result of hydrogen bonding. This is clearly evidenced in the net charges of Table II. Furthermore, it is suggested that the bonds of the pyridine ring tighten up, *i.e.*, the overlap populations in the ring increase on hydrogen bonding, which explains why the skeletal vibrations shift to higher frequencies.

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3. Nmr Chemical Shifts. It was also of interest to examine the effects of hydrogen bonding and protonation on the carbon-13 and nitrogen-14 chemical shifts of pyridine. For an atom of the second series, the paramagnetic shielding tensor (σ_{p}) is dominant.[43] Using LCAO MO theory it can be expressed in terms of orbital populations $\mathrm{p}_{\mu,\nu}$ and becomes[44]

$$\sigma_{\mathrm{p}} = \sigma_{\mathrm{o}}\{(\mathrm{p}_{xx} + \mathrm{p}_{yy} + \mathrm{p}_{zz}) - {}^1\!/_2(\mathrm{p}_{xx}\mathrm{p}_{yy} + \mathrm{p}_{yy}\mathrm{p}_{zz} + \mathrm{p}_{zz}\mathrm{p}_{xx}) + {}^1\!/_2(\mathrm{p}_{xy}\mathrm{p}_{yx} + \mathrm{p}_{yz}\mathrm{p}_{zy} + \mathrm{p}_{zx}\mathrm{p}_{xz})\}$$

where

$$\sigma_{\mathrm{o}} = -(2e^2\hbar^2/3\Delta m^2c^2)\langle r^{-3}\rangle$$

The details of these calculations can be found elsewhere.[45] The results for the carbon-13 chemical shifts, taking benzene as the relative standard, are given in Table III. Reasonable agreement between the calculated and experimental shifts is obtained.[21] In every case the correct sign of the shift is reproduced. Furthermore, the calculations clearly indicate that on hydrogen bonding the chemical shift of the carbon adjacent to the nitrogen atom shifts to higher values. The increase in the chemical shift is most pronounced in the pyridinium ion, where we have formed a full N-H σ bond. This agreement with experimental data, already hinted at from the higher electron density at the C_α position on protonation, is most gratifying and supports the qualitative validity of these calculations. This interesting phenomenon is quite general and has been observed in a large number of nitrogen heterocyclics. In each instance, the EHT method reproduces the experimental findings and these results will be summarized in a separate paper.[45]

Table III. Carbon-13 Chemical Shifts Relative to Benzene Using ΔE = 10 eV

System	Position	Calcd, ppm	Obsd,[21] ppm
Pyridine	2	−20.5	−21.72
	3	+2.9	+4.59
	4	−6.2	−7.42
Pyridine-water or methanol	2	−19.5	
	3	+1.5	
	4	−6.8	
Pyridinium ion	2	−18.6	−13.94
	3	−1.2	−0.45
	4	−6.9	−19.84

The results of the nitrogen-14 chemical shifts are given in Table IV. The low-field value of the nitrogen-14 shift for pyridine relative to the pyridinium ion is considered to be due to a larger paramagnetic contribution of the nitrogen lone-pair electrons.[46] The energy required to promote an electron to the excited state is less in pyridine than in the hydrogen-bonded or protonated pyridine molecule. On this basis, Gil and Murrell[47] have made a semiquantitative estimate of the change in the paramagnetic contribution for the nitrogen-14 shifts on protonation and found it to be −97 ppm which is in very good agreement with the observed value. As can be seen in column 2 of Table IV, the nitrogen-14 shifts calculated from EHT wave functions, using an average excitation energy of 10 eV, do not reproduce the proper sign nor relative ordering. Pople[48] considered the dominant local paramagnetic term and indicated three effects on the chemical shift: (a) linear charge dependence, (b) dependence on the mean electronic excitation energy, (c) effect of multiple bonds. In our calculations we have included effects a and c, but have left out effect b since we have used an average excitation energy of 10 eV for both pyridine and pyridinium ion. We have not taken into account the lower n → π* transition of pyridine compared to the pyridinium ion. In order to correct this, the nitrogen-14 shifts were recalculated using the transition energies obtained from EHT instead of an average energy of 10 eV.[45] The results are shown in column 3 of Table IV. The correct sign for the nitrogen-14 shifts is now obtained, but still the pyridinium ion shows a lower shift compared to pyridine, while the experimental value clearly indicates a higher shift.[7,46] This can probably be led back to poor transition energies and exaggerated charge separation, both deficiencies of the extended Hückel theory. It is evident that more work is necessary concerning the nitrogen-14 shifts.

Table IV. Nitrogen-14 Chemical Shifts Using the Ammonium Ion as Relative Standard

System	Calcd shifts, ppm ΔE = 10eV	$\Sigma\Sigma(E_j - E_i)^{-1}$	Obsd shifts,[7,46] ppm
Pyridine	129	−70	−280 ± 1
Pyridine–water	121	−72	. . .
Pyridine–methanol	121	−72	−271 ± 2
Pyridinium ion	22	−78	−169 ± 1.5

In conclusion, we feel that the extended Hückel theory gives an adequate account of hydrogen bonding in pyridine. The simplicity of the method makes it an attractive tool to examine a weakly bonded system like the hydrogen bond. The failures encountered in this study are readily led back to the well-known deficiencies of any Hückel theory, for example, poor energy levels and exaggerated charge separation. We are less surprised by the discrepancies between the calculated and experimental results than by the fact that such a simple treatment gives a reasonable account of the hydrogen bond.

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