

Molecular Orbital Theory of the Hydrogen Bond. 19.

Amide Hydrogen Bonding in Excited $n \rightarrow \pi^*$ States

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Abstract: Ab initio SCF-CI calculations have been performed to investigate the effect of hydrogen bonding on $n \rightarrow \pi^*$ transitions in 1:1 and 2:1 water-amide complexes containing the amide molecules formamide, methylformamide, acetamide, and methylacetamide. It has been found that hydrogen bonding leads to an increase in amide $n \rightarrow \pi^*$ transition energies in dimers. When the amide is the proton acceptor molecule, this increase is approximately equal to the ground state hydrogen bond energy, suggesting that the blue shift of the $n \rightarrow \pi^*$ band reflects the additional energy required to break the hydrogen bond in the excited state. In trimers in which the amide molecule is the central molecule acting as both a proton donor and proton acceptor, the blue shift of the $n \rightarrow \pi^*$ band is approximately equal to the sum of the blue shifts in the corresponding dimers. When the amide molecule is the terminal proton acceptor molecule in an open 2:1 water-formamide trimer, the blue shift increases owing to a stronger O-H \cdots O hydrogen bond at the carbonyl oxygen. Methyl substitution in formamide causes small changes in amide $n \rightarrow \pi^*$ transition energies, and has only an indirect effect on $n \rightarrow \pi^*$ transition energies of proton acceptor amide molecules in hydrogen-bonded complexes, insofar as it influences the ground state hydrogen bond energies.

Introduction

One of the more dramatic effects of hydrogen bond formation is the blue shift of the $n \rightarrow \pi^*$ band of molecules in hydrogen bonding solvents. Molecular orbital studies of this phenomenon have been able to reproduce this blue shift.¹⁻⁴ Moreover, in previous papers of this series,^{3,4} it has been demonstrated that the blue shift of the $n \rightarrow \pi^*$ band in dimers is approximately equal to the ground state hydrogen bond energy, provided that the $n \rightarrow \pi^*$ transition in the proton acceptor molecule is associated with electron excitation from an n orbital essentially localized at the proton acceptor atom. It has been concluded that in such dimers, the hydrogen bond is broken or at least severely weakened in the excited state.

The study of the effect of hydrogen bonding on $n \rightarrow \pi^*$ transitions has been extended in this work, which examines $n \rightarrow \pi^*$ transition energies, first in a series of amide molecules (formamide, methylformamide, acetamide, and methylacetamide), and then in their hydrogen-bonded complexes with water. The purposes of this study are to determine the effect of methyl substitution on amide $n \rightarrow \pi^*$ transition energies, and the relationship of the blue shift of the $n \rightarrow \pi^*$ band in 1:1 and 2:1 water-amide complexes to the ground state stabilization energy. The complexes considered include the hydrogen-bonded dimers and selected trimers investigated in the study of methyl substituent effects on amide hydrogen bonding in the ground state, a study reported in part 18 of this series.⁵ Thus, the present work extends that study to an investigation of these amide molecules and their hydrogen-bonded complexes with water in the excited $n \rightarrow \pi^*$ state.

Method of Calculation

Wave functions for the lowest energy singlet $n \rightarrow \pi^*$ state of the amide molecules and the 1:1 and 2:1 water-amide complexes have been obtained through configuration interaction (CI) calculations from the closed-shell ground state wave functions ${}^1\Psi^0$

$${}^1\Psi^0 = |\psi_1(1)\bar{\psi}_1(2) \cdots \psi_n(2n-1)\bar{\psi}_n(2n)|/\sqrt{(2n)!}$$

$$\equiv |1\bar{1} 2\bar{2} \cdots n\bar{n}|$$

determined with the STO-3G basis set⁶ in the study reported in part 18. The CI wave function ${}^1\Phi$, written as

$${}^1\Phi = \sum_i \sum_l A_{il} {}^1\Psi_i^l$$

is a linear combination of configurations ${}^1\Psi_i^l$, singly excited relative to the ground state, with the coefficients A_{il} determined variationally. The function ${}^1\Psi_i^l$ is defined as

$${}^1\Psi_i^l = [|1\bar{1} \cdots i\bar{l} \cdots n\bar{n}| - |1\bar{1} \cdots \bar{i}l \cdots n\bar{n}|]/\sqrt{2}$$

and describes the configuration which arises when an electron is promoted from orbital i , doubly occupied in the ground state, to virtual orbital l . In the CI expansion, the sums over i and l refer to valence occupied and virtual orbitals, respectively; thus, the CI results are essentially full first-order results. The CI energy of the singlet $n \rightarrow \pi^*$ state is the lowest eigenvalue of the full Hamiltonian matrix between the entire set of singly excited configurations. The $n \rightarrow \pi^*$ transition energies have been computed at the geometries of the monomers and hydrogen-bonded complexes described in part 18, and correspond to vertical $n \rightarrow \pi^*$ transition energies. All of the CI calculations have been performed in double precision on an IBM 370/145 computer.

Results and Discussion

Monomers. The $n \rightarrow \pi^*$ transition energies of the amide molecules formamide, methylformamide, acetamide, and methylacetamide are reported in Table I. As evident from these data, methyl substitution in formamide has only a small effect on $n \rightarrow \pi^*$ transition energies. Substitution of a methyl group at the nitrogen "s-cis" to CO lowers the $n \rightarrow \pi^*$ transition energy by 0.04 eV, while methyl substitution at the carbon increases the $n \rightarrow \pi^*$ transition energy by the same amount. Dimethyl substitution produces no change in the $n \rightarrow \pi^*$ transition energy.

Methyl substitution destabilizes both the n and π^* orbitals in the substituted formamides. In formamide, methylformamide, acetamide, and methylacetamide, respectively, the n orbital energies are -9.08, -8.96, -8.70, and -8.60 eV, and the π^* orbital energies are 8.90, 8.91, 9.00, and 9.01 eV. These data indicate that there is no quantitative relationship between orbital energies and $n \rightarrow \pi^*$ transition energies in this series of molecules. Similarly, there is no correlation between the CI state energies and the energies of the singly excited $n \rightarrow \pi^*$ configuration which is the dominant configuration in the lowest excited singlet state of each molecule, with a CI expansion coefficient greater than 0.97. The single configuration $n \rightarrow \pi^*$ transition energies are 5.69, 5.72, 5.92, and 5.92 eV in formamide, methylformamide, acetamide, and methylacetamide, respectively. These energies do not reflect the order of CI state

Table I. $n \rightarrow \pi^*$ Transition Energies, Blue Shifts, and Ground State Hydrogen Bond Energies in Amide-Water Dimers (eV)

	Transition energy	Blue shift	Hydrogen bond energy
Formamide	5.49		
Dimer A	5.53	0.04	0.28
B	5.52	0.03	0.28
E	5.71	0.22	0.22
F	5.73	0.24	0.28
Methylformamide	5.45		
Dimer A	5.48	0.03	0.27
B	5.48	0.03	0.27
E	5.66	0.21	0.23
F	5.64	0.19	0.21
Acetamide	5.53		
Dimer A	5.56	0.03	0.26
B	5.55	0.02	0.25
E	5.75	0.22	0.24
F	5.78	0.25	0.28
Methylacetamide	5.49		
Dimer A	5.51	0.02	0.25
B	5.50	0.01	0.24
E	5.72	0.23	0.24
F	5.69	0.20	0.22

energies in this closely related series of molecules. Thus, while the large CI coefficient of the $n \rightarrow \pi^*$ configuration justifies the labeling of these states as $n \rightarrow \pi^*$ states, CI is necessary for their description.

The electron distribution in the excited $n \rightarrow \pi^*$ state of these amide molecules is significantly different from the ground state, as indicated by the Mulliken electron populations⁷ reported in Table II. The major changes in the electron distribution are found within the carbonyl group, and are due to the nature of the dominant $n \rightarrow \pi^*$ configuration. In this configuration, an electron is removed from an n orbital which is primarily an oxygen p orbital in the molecular symmetry plane, and placed in an antibonding π orbital which has its main contribution from the carbon p orbital, a smaller contribution from the oxygen p , and a very small contribution from the nitrogen p , with nodes between oxygen and carbon, and between carbon and nitrogen. As a result of excitation, the carbonyl carbon becomes negatively charged owing to a large increase in the carbon π electron density. Although the oxygen π electron density also increases significantly, the carbonyl oxygen becomes positively charged owing to an even greater loss of σ electron density. Smaller changes in electron populations are found at the nitrogen atom, which experiences a slight increase in negative charge owing to an increase in the nitrogen π electron density. The change in the electron distribution in the excited $n \rightarrow \pi^*$ state is also apparent from the excited state dipole moments which are reduced from the ground state values of 2.64–2.70 D, to 0.31–0.44 D, with a near reversal in direction.

Dimers. The $n \rightarrow \pi^*$ transition energies in the 1:1 water-amide dimers A, B, E, and F are reported in Table I. Also reported are the increases in the $n \rightarrow \pi^*$ transition energies in the dimers (the “blue shifts” of the $n \rightarrow \pi^*$ bands), and the dimer ground state hydrogen bond energies. As evident from these data, association of a water and an amide molecule through hydrogen bonding leads to an increase in the $n \rightarrow \pi^*$ transition energy in these amide molecules. When the amide is the proton donor molecule in the complex, this increase is quite small, ranging from 0.01 eV in the methylacetamide-water dimer B to 0.04 eV in the formamide-water dimer A. Since the $n \rightarrow \pi^*$ transition is associated with the carbonyl group in these molecules, it is not surprising that hydrogen bonding through the N–H proton has little effect on the $n \rightarrow \pi^*$ transition energy in dimers A and B. In contrast, when the carbonyl oxygen is hydrogen bonded as the proton acceptor atom in dimers E and F, large blue shifts of the $n \rightarrow \pi^*$ band are found. Of particular significance is the relationship between the blue shift of the $n \rightarrow \pi^*$ band and the ground state hydrogen bond energy. As the data of Table I illustrate, the blue shift of the $n \rightarrow \pi^*$ band is within 0.02 eV of the ground state hydrogen bond energy in each amide-water dimer which has an open structure. In the cyclic formamide-water and acetamide-water F dimers, the blue shifts are only 0.04 and 0.03 eV smaller than the ground state stabilization energies, respectively. These data are consistent with previous results which also show that the blue shift of the $n \rightarrow \pi^*$ band is approximately equal to the ground state hydrogen bond energy in dimers in which the $n \rightarrow \pi^*$ transition removes an electron from an n orbital which is essentially localized at the proton acceptor site.^{3,4} They indicate that the hydrogen bond is broken or at least severely weakened in the $n \rightarrow \pi^*$ state of such complexes, and suggest that vibrational relaxation would lead to dissociation. That an excited amide molecule would no longer be hydrogen bonded through the carbonyl oxygen as in the ground state is a direct consequence of the electron redistribution which occurs upon excitation to the $n \rightarrow \pi^*$ state. Since a correlation between the hydrogen bond energy and the blue shift of the $n \rightarrow \pi^*$ band is apparent in each of these dimers, it may also be concluded that methyl substitution in formamide has only an indirect effect on the dimer $n \rightarrow \pi^*$ transition energy insofar as the methyl group influences the ground state stabilization energy.

In their studies of hydrogen bonding, Kollman and Allen first noted that hydrogen bonding stabilizes the orbitals of proton acceptor molecules.⁸ This observation has been supported by recent data from photoelectron spectroscopy, which show that the ionization potential of the electron pair involved in an intramolecular hydrogen bond is higher than in a geometrical isomer in which hydrogen bonding is precluded.⁹ While the blue shift of the $n \rightarrow \pi^*$ band was originally attributed to the stabilization of the n orbital,¹⁰ it was later discussed by Pimentel in terms of the solvation of the ground and excited states.¹¹ In previous studies in this laboratory,³ it has been demonstrated that the blue shift of the $n \rightarrow \pi^*$ band cannot be

Table II. Mulliken Total and π Electron Populations in Ground and Excited $n \rightarrow \pi^*$ States of Amide Molecules^a

	O		C ^b		N		H ^c
	Total	π^d	Total	π^d	Total	π^d	
Formamide	7.779 (8.267)	1.625 (1.250)	6.294 (5.745)	1.450 (0.899)	7.453 (7.438)	1.926 (1.851)	0.799 (0.804)
Methylformamide	7.781 (8.268)	1.624 (1.249)	6.297 (5.753)	1.451 (0.906)	7.380 (7.366)	1.897 (1.824)	0.805 (0.810)
Acetamide	7.788 (8.280)	1.631 (1.264)	6.224 (5.684)	1.428 (0.855)	7.453 (7.442)	1.930 (1.862)	0.804 (0.809)
Methylacetamide	7.789 (8.280)	1.630 (1.263)	6.228 (5.692)	1.430 (0.892)	7.380 (7.371)	1.901 (1.834)	0.809 (0.814)

^a Ground state populations in parentheses. ^b The carbonyl carbon. ^c The N–H proton “s-trans” to CO. ^d π refers to atomic p orbitals perpendicular to the molecular symmetry plane.

interpreted simply in terms of the stabilization of the n orbital, since no quantitative relationship has been found between these two properties. Even in the amide-water dimers where similar methyl-substituted formamide molecules are hydrogen bonded to water, no simple correlation exists between changes in n orbital energies and $n \rightarrow \pi^*$ transition energies. As expected, both the n and π^* orbitals are stabilized in dimers with the amide molecules as proton acceptors. In the open E dimers, the n orbital is stabilized by 0.35 eV in the formamide-water and methylformamide-water dimers, and by 0.36 eV in the acetamide-water and methylacetamide-water dimers. In the open methylformamide-water and methylacetamide-water F dimers, hydrogen bonding has a slightly greater stabilizing effect on the n orbital (0.38 and 0.40 eV, respectively), even though the $n \rightarrow \pi^*$ transition energies in these dimers are less than in the corresponding E dimers. In the formamide-water and acetamide-water F dimers, hydrogen bonding stabilizes the n orbital by only 0.05 and 0.11 eV, respectively; it is in these cyclic dimers that the largest blue shifts of the $n \rightarrow \pi^*$ band are found. It is also interesting to note that while hydrogen bonding causes a slight increase in $n \rightarrow \pi^*$ transition energies in dimers having the amide molecules as proton donors, it has a large destabilizing effect on the n and π^* orbitals. For example, in dimers A and B, the destabilization of the n orbital ranges from 0.48 eV in the methylacetamide-water dimer B to 0.67 eV in the formamide-water dimer A.¹²

Trimers. In the study of the effect of hydrogen bonding on $n \rightarrow \pi^*$ transition energies in 2:1 water-formamide open trimers A-E and B-E in which formamide is both a proton donor and proton acceptor molecule, it was found that the blue shift of the $n \rightarrow \pi^*$ band could be approximated as the sum of the blue shifts of the $n \rightarrow \pi^*$ bands in dimers A and E, and B and E, respectively.⁴ The data of Table III indicate that this approximate additivity of blue shifts occurs in the entire set of trimers A-E, B-E, A-F, and B-F which have substituted amide molecules as proton donors and proton acceptors. Thus, this additivity is independent of methyl substitution in the amide molecule, and of the open or closed structure of the constituent amide-water dimers.

When the amide molecule is the central molecule in 2:1 water-amide trimers A-E, B-E, A-F, and B-F, trimer formation has a destabilizing effect on the amide n orbital relative to the monomer. This destabilization appears to be the net result of the opposing effects of hydrogen bonding on the n orbitals of proton donor and proton acceptor molecules. As noted above, this orbital in the amide proton acceptor molecule is stabilized in dimers E and F, but is destabilized to an even greater extent in the proton donor amide molecules in dimers A and B. The destabilization of the amide n orbital in trimers emphasizes once again that blue shifts of $n \rightarrow \pi^*$ bands in hydrogen-bonded complexes are not simply related to n orbital energy changes.

The investigation of the $n \rightarrow \pi^*$ transition energies in 2:1 water-amide trimers has now been extended to the 2:1 water-formamide trimers AWW-A and WWA-E which have open structures. In AWW-A, the formamide molecule acts only as a proton donor to a hydrogen-bonded water dimer. The computed $n \rightarrow \pi^*$ transition energy in this trimer is 5.53 eV, which is equal to the $n \rightarrow \pi^*$ transition energy in dimer A. Thus, it appears that even though trimer AWW-A is 0.11 eV more stable than the corresponding dimers and the hydrogen bond energies are nonadditive by 0.09 eV, the strengthening of the hydrogen bonds in the N-H...O-H...O chain has no effect on the $n \rightarrow \pi^*$ transition, which is associated with electron excitation from a non-hydrogen-bonded carbonyl oxygen. In contrast, the $n \rightarrow \pi^*$ transition energy in the open trimer WWA-E is 5.76 eV, which is an increase of 0.05 eV compared to dimer E. As the data of part 18 indicate, the nonadditivity of hydrogen bond energies in this trimer is 0.08 eV. A parti-

Table III. $n \rightarrow \pi^*$ Transition Energies of Selected Trimers (eV)

	Transition energy	Blue shift	Sum of dimer blue shifts
Methylformamide			
Trimer A-E	5.71	0.26	0.24
B-E	5.71	0.26	0.24
A-F	5.68	0.23	0.22
B-F	5.68	0.23	0.22
Acetamide			
Trimer A-E	5.80	0.27	0.25
B-E	5.78	0.25	0.24
A-F	5.83	0.30	0.28
B-F	5.81	0.28	0.27
Methylacetamide			
Trimer A-E	5.76	0.27	0.25
B-E	5.75	0.26	0.24
A-F	5.73	0.24	0.22
B-F	5.72	0.23	0.21

tioning of this additional energy between the two hydrogen bonds is suggestive of the origin of the 0.05-eV blue shift of the $n \rightarrow \pi^*$ band relative to dimer E. Thus, it appears that the stronger O-H...O hydrogen bond at the carbonyl oxygen in the O-H...O-H...O chain is reflected in an increased blue shift of the $n \rightarrow \pi^*$ band in this open trimer relative to the corresponding dimer E.

Conclusions

The conclusions which may be drawn from this study are summarized as follows.

1. Association of an amide molecule and a water molecule through hydrogen bonding leads to an increase in the amide $n \rightarrow \pi^*$ transition energy. This increase is significant only in dimers in which the amide molecule is the proton acceptor molecule. In these dimers, the blue shift of the $n \rightarrow \pi^*$ band is approximately equal to the ground state hydrogen bond energy, suggesting that the hydrogen bond is broken, or at least severely weakened, in the excited state. No simple relationship exists between dimer blue shifts of $n \rightarrow \pi^*$ bands and changes in n orbital energies due to hydrogen bonding.

2. Dimer blue shifts of $n \rightarrow \pi^*$ bands are approximately additive in trimers in which the amide molecule is both a proton donor through the N-H proton and proton acceptor through the carbonyl oxygen.

3. When the amide molecule is the terminal proton acceptor molecule in an open 2:1 water-formamide trimer, the blue shift of the $n \rightarrow \pi^*$ band is larger than in the corresponding dimer. This appears to be a direct consequence of the formation of a stronger hydrogen bond at the carbonyl oxygen in the O-H...O-H...O chain of hydrogen bonds.

4. Methyl substitution in formamide leads to small changes in the $n \rightarrow \pi^*$ transition energy of amide molecules, and has only an indirect effect on the blue shift of the $n \rightarrow \pi^*$ band of proton acceptor amide molecules in amide-water complexes, insofar as it influences the ground state hydrogen bond energy.

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A Theoretical Study of Proton Addition to Oxirane, Aziridine, and 2-Azirene

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Abstract: We have performed an ab initio study on the influence of protonation on the structure of some three-membered rings, using an extended basis set. According to our results no shortening of the C-C bond takes place upon protonation. The protonation energies calculated using the optimized geometries or those obtained from the electrostatic potential of the neutral molecules are in good agreement with experimental values.

I. Introduction

Protonation of organic molecules has been the subject of many experimental¹⁻¹⁰ and theoretical¹¹⁻¹⁹ studies in the last 7 years. Some factors involved in the protonation process (effects of hybridization,⁷ substituent effects,^{5b,8b,19} polarization¹⁵ and solvation^{8b} effects, etc.) have also been investigated.

In most calculations the geometry of the protonated species was determined by means of electrostatic potential maps.^{12,15,16,18} This simple treatment is qualitatively valid¹⁵ as a first-order prediction of protonation sites and affinities. It is, in general, accepted that the bare proton perturbs the molecule to a considerable extent. However, the effect of protonation on molecular geometry and electrostatic potentials (therefore on the protonation energies calculated) has not been well studied.

Three-membered rings have received particular attention mainly because their size make them very suitable for ab initio calculations.

Protonation is sometimes followed by ring opening leading to different recombination products.²⁰ Stohrer and Hoffmann¹⁴ postulated that protonation or other coordination of the heteroatom lone pair, in oxiranes and aziridines, strengthens the C-C bond. However, this theoretical conclusion is not in complete agreement with experimental results. The structure of aziridinium salts²¹ show no shortening of the C-C bond and when aziridine forms a coordination compound with borane, the shortening of the C-C bond (from 1.48 Å²² to 1.46 Å²³) is not significant.

In this paper we present the results of an ab initio study of the effects of protonation on the structure of oxirane and aziridine (the first member of each family) and 2-azirene. We also investigate the influence of geometry on the calculated electrostatic potentials and the proton affinity values obtained by computing the SCF energy with the proton placed at the position of the electrostatic potential minimum.

II. The Effect of Protonation on Geometry

To establish the effects of protonation on a given molecule it is necessary to know the structure of the neutral and protonated species. We use experimental geometries for neutral oxirane and aziridine. Since experimental information on the structure of 2-azirene and all the protonated species is not available we have chosen the SCF optimized geometry for those species. This procedure leads, in general, to geometries in good agreement with the experimental ones.²⁴

In order to save computation time the optimization process was divided into two parts: (a) full optimization with a (STO-3G) minimal basis set²⁵ and (b) full optimization of the geometry of neutral molecules using the final result of (a), as a starting point, and a split-valence (6-31G) basis set.²⁶ For the protonated species only those parameters directly involved in the possible shortening of the C-C bond (CXC angle and CX bonds) were optimized in this step.

Figure 1a contains the results of part (a) for aziridine²⁷ along with experimental values (in parentheses) determined by microwave spectroscopy.²² The agreement is excellent. We have found²⁷ that the dihedral angle between the CH₂ groups and the ring is 87°. This value is also found in the most recent microwave studies.²² These planes do not bisect the NCC angle, but divide it into two parts (see Figure 1c), $\alpha = 33.6^\circ$ and $\beta = 26.5^\circ$, again in good agreement with experimental values;²² $\alpha = 33.7^\circ$, $\beta = 26.2^\circ$.

Step (b) introduces no significant changes in the geometry obtained in (a). The most important one is the change in γ (Figure 1a), whose value is now 61°.

The results of Figure 1b correspond to the protonated molecule. It is clear that some changes have taken place. γ decreases by 9°, owing to the change in the nitrogen atom, when the second proton is bound to the lone pair.

The changes in the ring affect mainly the CNC angle that