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Ab Initio Study of the Hydrogen-Bonded Bridging NH_3:Pyridone Complex

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Abstract: Ab initio calculations have been carried out at the MP2/6-31+G(d,p) level of theory to determine the equilibrium structure of the NH_3:pyridone complex in the N—H and C=O region of pyridone. The NH_3 molecule is both a proton donor and a proton acceptor in this complex, which is stabilized by nonlinear N—H···N and N—H···O hydrogen bonds. Computed and experimental rotational constants for NH_3:pyridone and the barrier to rotation of the NH_3 molecule are in good agreement. There is also good agreement between the computed and the experimental structure of the NH_3:pyridone complex in the region of the N—H···N hydrogen bond in which NH_3 is the proton acceptor molecule. However, differences are found between the experimental and the computed descriptions of the N—H···O hydrogen bond in which NH_3 is the proton donor. In particular, the experimental structure has an N—H···O hydrogen bond which deviates from linearity to a much greater extent and a very long H···O distance. Sources of this discrepancy are discussed. The electronic binding energy of the NH_3:pyridone complex at MP2/cc-pVTZ+//MP2/6-31+G(d,p) is 10.9 kcal/mol, leading to a room temperature binding enthalpy of 9.3 kcal/mol. The NH_3:pyridone complex is approximately 1 kcal/mol less stable than the corresponding H_2O:pyridone complex.

Introduction

In two recent papers, Held and Pratt reported the results of studies of the rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectra of the mono- and disolvated water complexes of 2-pyridone[1] and of the corresponding complexes of ammonia with 2-pyridone.[2] Using the experimental structures of the monomers and their own experimental data, these authors were able to deduce a set of intermolecular structural parameters for gas-phase H_2O:pyridone, $(H_2O)_2$:pyridone, NH_3:pyridone, and $(NH_3)_2$:pyridone complexes by iteratively fitting computed rotational constants to the experimental constants for these complexes. At the time when their work was done, the best ab initio calculations available on these complexes were those reported by Field and Hillier,[3] which had been carried out at the HF/3-21G level of theory. The experimental and the computed structural data were not in good agreement.

This situation prompted an investigation of the H_2O:pyridone and $(H_2O)_2$:pyridone complexes in this laboratory.[4] Our recent work had demonstrated that structures optimized at the MP2/6-31+G(d,p) level of theory yield intermolecular distances and hydrogen-bonded X—H stretching frequency shifts in good agreement with experimental data.[5-8] Moreover, single-point calculations at these geometries carried out at MP2 with the Dunning correlation-consistent polarized valence triple-split basis set augmented with diffuse functions on non-hydrogen atoms provide reliable binding energies.[5-8] The optimized MP2/6-31+G(d,p) structures of the H_2O:pyridone and $(H_2O)_2$:pyridone complexes are in good agreement with the experimental structures of Held and Pratt, providing further support for the experimental structures and for the assumptions that had been made in the process of resolving them.

In their discussion of the NH_3:pyridone complex, Held and Pratt[2] suggested that NH_3 acts as both a proton donor and a proton acceptor in the N—H and C=O region, noting that their data provided the first evidence of a single gas-phase molecule acting in both capacities for hydrogen bonding. Their primary evidence that NH_3 acts as a proton donor was the observation of a large barrier of 424 cm^{-1} (about 1.2 kcal/mol) to internal rotation of NH_3 in the ground state, which is considerably greater than barriers observed in other N—H···NH_3 complexes.[2] However, they also commented that, on the basis of a distance criterion, the long distance between the carbonyl oxygen and the hydrogen-bonded hydrogen of ammonia found in their structure suggests that the interaction between these atoms must be very weak, if it exists at all.

In the present paper, computed energetic and structural data for the NH_3:pyridone complex will be reported and compared with the corresponding experimental data given by Held and Pratt.[2] Of particular interest is the description of the N—H···O hydrogen bond, in view of the large barrier to NH_3 rotation measured by Held and Pratt despite the long H···O distance. The computed results provide further insight into the nature of the N—H···O interaction. The computed binding energy of this complex will be compared with the computed binding energy of the corresponding H_2O:pyridone complex.

Methods

The structure of the NH_3:pyridone complex which exists in the N—H and C=O region of the surface has been fully optimized with correlation at second-order many-body Møller–Plesset perturbation theory [MBPT-(2) = MP2][9-12] using the split-valence plus polarization 6-31+G(d,p) basis set[13,14] augmented with diffuse functions on non-hydrogen atoms.[15,16] Harmonic vibrational frequencies at MP2/6-31+G(d,p) were

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computed to confirm that the resulting structure is an equilibrium structure (a local minimum with no imaginary frequencies) and to evaluate zero-point and thermal vibrational energies. To estimate the rotational barrier of NH_3 in this complex, a second NH_3:pyridone structure was generated from the equilibrium structure through rotation of NH_3 by 180° about a local pseudo-C_3 axis. This new structure, in which two hydrogens of NH_3 interact with the carbonyl oxygen in a "bifurcated" arrangement, was then fully optimized under the constraint of C_s symmetry. The MP2/6-31+G(d,p) structures of the monomers NH_3 and pyridone were already available.

The binding energy of the equilibrium NH_3:pyridone complex was computed from total energies obtained from single-point calculations performed at the MP2 level of correlation using an augmented Dunning correlation-consistent polarized valence triple-split basis set.[17] The Dunning polarized triple-split valence basis includes in the polarization space two sets of d functions and one set of f functions on C, N, and O. This basis was augmented with a set of diffuse s and p functions, with exponents 0.04, 0.06, and 0.08 for C, N, and O, respectively. The corresponding Dunning basis for hydrogen has three s functions, two sets of p functions, and one set of d functions, but no diffuse functions. This augmented basis set is denoted cc-pVTZ+. Studies in this laboratory with the Dunning basis sets and previous work show that diffuse functions on hydrogens are not significant energetically.[18,19] Details of this basis set, its performance in the calculation of hydrogen bond energies, and the appropriateness of the MP2/cc-pVTZ+//MP2/6-31+G(d,p) level of theory for describing neutral hydrogen-bonded complexes are given in previous papers.[5-8]

Geometry optimizations and single-point calculations were done freezing electrons below the valence shells in the Hartree–Fock MOs. Binding enthalpies at room temperature were computed from the MP2/cc-pVTZ+//MP2/6-31+G(d,p) electronic binding energies, MP2/6-31+G(d,p) zero-point vibrational energies, and other thermal terms. All calculations were performed at the Ohio Supercomputer Center using the Gaussian 92 system of computer programs[20] on a Cray Y-MP8/864 computer.

Results and Discussion

The equilibrium structure of the NH_3:pyridone complex in the N—H and C═O region of the intermolecular surface is shown in Figure 1. Table 1 presents the computed MP2/6-31+G(d,p) binding energy and selected intermolecular structural data for this complex, along with the corresponding structural data from ref 2. Computed and experimental rotational constants are given in Table 2. Table 3 presents computed changes in selected intramolecular coordinates of NH_3 and pyridone upon complex formation.

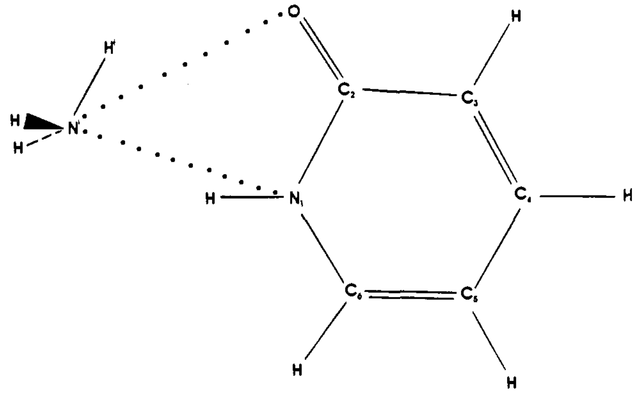

Figure 1. The equilibrium NH_3:pyridone complex in the N—H and C═O region. The C_s symmetry plane of pyridone is the symmetry plane for the complex.

Table 1. MP2/6-31+G(d,p) Binding Energy and Selected Intermolecular Structural Data for the Equilibrium NH_3:Pyridone Complex[a]

	computed	exptl[b]
ΔE	12.0	
N—H...N′ bond		
R(N—N′)	2.91	2.94 ± 0.02
R(H—N′)	1.94	1.99 ± 0.03
∠(H—N—N′)	16	
∠(N—H—N′)	156	154.2 ± 3
∠(N′—N—C_2)	98.6	96.9 ± 0.3
N′—H′—O bond		
R(N′—O)	3.05	
R(H′—O)	2.22	2.91 ± 0.1
∠(H′—N′—O)	30	
∠(N′—H′—O)	137	87.2 ± 10
∠(N′—O═C)	96	

[a] Binding energy (ΔE) in kcal/mol; distances in angstroms; angles in degrees. [b] Experimental data from ref 2.

Table 2. Computed MP2/6-31+G(d,p) and Experimental Ground State Rotational Constants (MHz)

	computed			exptl[a]		
	A	B	C	A	B	C
pyridone	5662	2763	1857	5644	2793	1869
NH_3:pyridone	3688	1389	1014	3725	1381	1013

[a] Data for pyridone from the following: Held, A.; Champagne, B. B.; Pratt, D. W. *J. Chem. Phys.* **1991**, *95*, 8732. Data for NH_3:pyridone from ref 2.

Table 3. Computed Changes in Intramolecular Bond Lengths and Bond Angles in the NH_3:Pyridone Complex[a]

NH_3	
hydrogen-bonded N′—H′	0.008
non-hydrogen-bonded N′—H	0.002
∠H′—N′—H	−0.1
∠H—N′—H	−0.9
pyridone	
N—H	0.018
C═O	0.009
N_1—C_2	−0.006
∠N—C═O	0.3

[a] Distances in angstroms; angles in degrees. A negative sign indicates a decrease in the coordinate in the complex relative to the isolated monomer.

The equilibrium NH_3:pyridone complex in the N—H and C═O region of pyridone has a bridging structure with NH_3 acting as both a proton donor to pyridone at the carbonyl oxygen and a proton acceptor from the N—H of pyridone. This complex is stabilized by two distorted N′—H′···O and N—H···N′ hydrogen bonds (see Figure 1). The MP2/cc-pVTZ+ binding energy of this complex is 10.9 kcal/mol, with a zero-point destabilization energy of 2.0 kcal/mol. The binding enthalpy of this complex at room temperature is 9.3 kcal/mol. Thus, this complex is about 1 kcal/mol less stable than the corresponding H_2O:pyridone complex in the same region of pyridone.[4] The computed moments of inertia for pyridone and the NH_3:pyridone complex at their optimized MP2/6-31+G(d,p) geometries are reported in Table 2, along with the experimental

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moments given by Held and Pratt.[2] As evident from this table, there is good agreement between the computed and the experimental values.

Table 1 reports the optimized MP2/6-31+G(d,p) structure of the NH_3:pyridone complex and the experimental structure of Held and Pratt which they determined by changing intermolecular coordinates and iteratively fitting computed rotational constants to the experimentally measured constants.[2] The computed structure of the NH_3:pyridone complex has an N−N′ distance of 2.91 Å, an H−N′ distance of 1.94 Å, an N−H−N′ angle of 156°, and an $N'-N-C_2$ angle of 98.6°. As evident from Table 1, these values are in quite good agreement with the experimentally determined values. Thus, there is good agreement between the computed structure and the experimental structure of the NH_3:pyridone complex in the region of the N−H··N′ hydrogen bond in which NH_3 is the proton acceptor.

There is disagreement between the computed and the experimental structures of the NH_3:pyridone complex in the region of the N′−H′··O hydrogen bond in which NH_3 is the proton donor. This difference arises from a difference in the in-plane tilt of the NH_3 molecule. In the computed structure the N′−H′−O angle is 137° (the angle between the N′−H′ bond and the hydrogen-bonding N′−O axis is 30°), giving an H′−O distance of 2.22 Å. In contrast, the experimental structure of NH_3:pyridone given by Held and Pratt[2] has an N′−H′−O angle of 87.2 ± 10°, which leads to a very nonlinear hydrogen bond with a long H′−O distance of 2.91 ± 0.1 Å. It was this distance which led these authors to comment that the N′−H′−O interaction must be weak, if it even exists. The NH_3 orientation which gives rise to this very nonlinear hydrogen bond in the structure of Held and Pratt is a result of their observation that the C_3 rotational axis of an assumed undistorted NH_3 molecule must be essentially parallel (within 10°) to the *a* inertial axis of the complex in order to fit the spectra.

To estimate the energetic consequences of such an in-plane tilt of the NH_3 molecule in the experimental structure, an MP2/6-31+G(d,p) calculation was performed on a complex in which all coordinates were set at the values obtained for the fully optimized MP2/6-31+G(d,p) structure, except for the NH_3 molecule, which was tilted so that the N′−H′−O angle (90°) matched the value given by Held and Pratt.[2] This change in the NH_3 orientation reduces the stability of this complex by 5.4 kcal/mol relative to the equilibrium complex. Thus, this is not an insignificant change. Closer examination of this structure shows that this orientation of NH_3 significantly disrupts the N′−H′··O hydrogen bond, as the angle between the N′−H′ bond and the N′−O line increases from 30° to 70°. Moreover, it also weakens the N−H··N′ hydrogen bond. If it is assumed that the lone pair on the nitrogen of NH_3 points approximately in one of the sp^3 directions, then this orientation directs that lone pair toward the N_1-C_2 bond of pyridone, rather than toward the proton donor N−H. This directional change significantly weakens the N−H··N′ hydrogen bond as well.

It is appropriate at this point to search for the source of the discrepancy between the computed and the experimental descriptions of the structure of the NH_3:pyridone complex in the N′−H′··O region. Is the H′··O distance in the computed structure too short due to an overestimation of the strength of the N′−H′··O interaction? Some insight into this possibility may be gained by examining the energy of the optimized structure of the NH_3:pyridone complex in which two N−H's interact with the carbonyl oxygen in a "bifurcated" arrangement. This structure would be a transition structure for interchanging hydrogen-bonded N−H's of NH_3. On the MP2/6-31+G(d,p) surface, this structure is 1.1 kcal/mol higher in energy than the equilibrium structure. This result is in excellent agreement with the experimental NH_3 rotational barrier of 1.2 kcal/mol determined by Held and Pratt.[2] Hence, both theory and experiment are in agreement concerning the energetics of this aspect of the N′−H′··O interaction.

A second possible source of the discrepancy between theory and experiment is the orientation of the local C_3 axis of NH_3. From their data, Held and Pratt[2] concluded that this axis is essentially parallel (within 10°) to the *a* inertial axis of the complex. It is the orientation of this axis which is responsible for the in-plane tilt of the NH_3 molecule which leads to the very nonlinear N′−H′··O bond and the long H′··O distance. In the computed structure there is no local C_3 axis of NH_3 because of small changes in intramolecular NH_3 coordinates upon complex formation. However, it is possible to approximate the position of a pseudo-C_3 local axis in the computed structure. This axis was found to make an angle of about 7° with the computed *a* inertial axis of the complex and is therefore within the limits determined by Held and Pratt.

The third possible source of the discrepancy between theory and experiment in describing the N′−H′··O hydrogen bond may be in the assumption of Held and Pratt that the experimental monomer coordinates of NH_3 and pyridone are unchanged in the complex. The computed changes in the intramolecular coordinates of the NH_3 and pyridone subunits upon formation of the NH_3:pyridone complex are given in Table 3. While these changes are small, they do occur, and they contribute to the definition of the inertial axes. These axes are oriented slightly differently in the computed structure compared with the experimental one. It may be that the increase in the N−H bond lengths and the decrease in the H−N−H angles of NH_3 are primarily responsible for the discrepancy between the experimental and theoretical descriptions of the N′−H′··O hydrogen bond. Since the NH_3 molecule lies relatively far from the inertial axes, small changes in NH_3 coordinates may have a disproportionately large effect.

With only two exceptions, changes in intramolecular coordinates in the NH_3:pyridone complex in the hydrogen-bonding region are smaller than changes in the corresponding intramolecular coordinates in the H_2O:pyridone complex. One exception occurs for the lengths of non-hydrogen-bonded O−H and N−H bonds of H_2O and NH_3, respectively. In the H_2O:pyridone complex, the non-hydrogen-bonded O−H bond length is unchanged upon complex formation, whereas the non-hydrogen-bonded N−H bonds of NH_3 increase by 0.002 Å in the complex. Different changes in bond angles also occur in H_2O and NH_3, since the H−O−H angle of H_2O increases upon complexation with pyridone, whereas H−N−H angles of NH_3 decrease upon complexation. Another exception to the generalization that changes in intramolecular coordinates in the NH_3:pyridone complex are smaller than in the corresponding H_2O:pyridone complex is found for the pyridone N−H bond length. In the H_2O:pyridone complex the length of the pyridone N−H bond increases by 0.010 Å, but in the NH_3:pyridone complex it increases by 0.018 Å. This suggests that the N−H··N hydrogen bond is stronger than the corresponding N−H··O hydrogen bond. The computed MP2/6-31+G(d,p) structural data also suggest that the hydrogen bond to the carbonyl oxygen of pyridone is weaker in NH_3:pyridone than in H_2O:pyridone. In NH_3:pyridone the N′−H′··O hydrogen bond deviates from linearity by 30°. In H_2O:pyridone the deviation from linearity of the O−H··O hydrogen bond is significantly less at 13°.

Conclusions

The computed MP2/6-31+G(d,p) equilibrium NH_3:pyridone complex in the N−H and C=O region of pyridone has a bridging structure stabilized by two distorted N—H···N' and N'—H'···O hydrogen bonds. The computed rotational constants for this complex are in good agreement with the experimentally determined constants. At MP2/cc-pVTZ+//MP2/6-31+G(d,p), this complex has an electronic stabilization energy of 10.9 kcal/mol, a 0 K stability of 8.9 kcal/mol, and a room temperature stabilization enthalpy of 9.3 kcal/mol. Thus, this complex is about 1 kcal/mol less stable than the corresponding H_2O:pyridone complex. The computed structure of the NH_3:pyridone complex in the region of the N—H···N' hydrogen bond with NH_3 as the proton acceptor is in good agreement with the experimental structure. However, the computed structure in the region of the N'—H'—O bond differs from the experimental structure, which has an N'—H'···O hydrogen bond that is very nonlinear and an unusually long H'···O distance. These structural differences may result from the assumption made in the determination of the experimental structure that monomer geometries are unchanged upon complex formation. Despite structural differences in the description of the N'—H'···O hydrogen bond, theory and experiment agree that the barrier to NH_3 rotation in this complex is about 1.2 kcal/mol.

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