Photoinduced Electron and Proton Transfer in the Hydrogen-Bonded Pyridine−Pyrrole System

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Received: April 16, 2007

We present here a detailed analysis of the mechanism of photoinduced electron and proton transfer in the planar pyrrole−pyridine hydrogen-bonded system, a model for the photochemistry of hydrogen bonds in DNA base pairs. Two different crossings, an avoided crossing and a conical intersection, are the key steps for forward and backward electron and proton transfer providing to the system photostability against UV radiation by restoring the system in its initial electronic and geometric structure.

It has been proposed that the coupled transfer of an electron and a proton along hydrogen bonds can lead to ultrafast deactivation of excited electronic states in DNA base pairs via conical intersections (CI) of charge-transfer (CT) states with locally excited states and the electronic ground state.[1] This particularly efficient mechanism of energy dissipation could be essential for the photostability of the molecular encoding of the genetic information of life.[2]

The exploration of the mechanistic details of excited-state deactivation processes in isolated DNA base pairs is impeded both in experiments as well as in theory by several factors. On the experimental side, there is the difficulty of bringing intact base pairs into the gas phase, the existence of multiple conformers, as well the existence of competitive processes such as ultrafast internal conversion within the individual bases.[2b,3] On the computational side, DNA base pairs pose considerable difficulties due to the large number of electrons and nuclear degrees of freedom and the existence of numerous closely spaced exited electronic states.[1] Simplified mimetic models of DNA base pairs which allow the investigation of specific photochemical processes without these complexities are therefore of considerable interest.[2a,4]

We present here a detailed analysis of the mechanism of photoinduced proton transfer in the planar pyrrole−pyridine hydrogen-bonded system. This system can be considered as a model of the "N−H···N" hydrogen bond in the guanine/cytosine (G/C) and adenine/thymine (A/T) Watson−Crick base pairs, and is itself an important system in the photochemistry of N hydrogen-bonded systems. The potential energy surfaces (PESs) of the relevant electronic states of this model system have been explored with the CASSCF//CASPT2 methodology.[5] Some distinctive characteristics have been found for this system. An S_2/S_1 avoided crossing (AC) region is responsible for the

electron-transfer process from pyrrole to pyridine after the local electronic excitation of the latter, followed by proton transfer in the excited state. The dramatic energetic stabilization of the CT state by the proton transfer leads to an S_1/S_0 conical intersection which is responsible for the ultrafast decay to the ground state via backward electron transfer and adiabatic proton back-transfer on the ground-state surface, restoring the system in its initial structure (see Figure 1).

In more detail, the photochemical mechanism can be described as follows. The optical excitation occurs to the lowest $^1\pi\pi^*$ excited state[6] (S_1; 4.95 eV for the vertical transition and 4.52 eV for the 0−0 transition).[7] This lowest excited state (1^1B_2) corresponds to a single excitation (HOMO-2 → LUMO) of the pyridine molecule[8] (see Figure 2). The vibrational excess energy is relatively small (5.4 kcal/mol) and is mainly associated with the stretching coordinates.

The S_2/S_1 crossing is of the AC type, since the gradient difference (GD) and derivative coupling (DC) vectors are parallel.[9] It is related to the electron transfer from pyrrole to pyridine, since the S_2 state is a $\pi\pi^*$ charge-transfer state (see Figure 2).[10] The electronic coupling, determined as the half energy gap at the AC, is 78 cm^{-1}, indicating a weak coupling of these states and therefore a diabatic character of the electron-transfer (ET) process.[11] Nevertheless, the low activation energy needed to reach the crossing (9.8 kcal/mol) indicates efficient population transfer to the CT state. Moreover, this transition is enhanced by the tunneling effect, since the reaction coordinate is associated with high-frequency modes stretching in both molecules.

By computing the minimum energy path (MEP) from the S_2/S_1 crossing in both directions of the DC vector, a barrierless path is found connecting the S_2/S_1 crossing with the S_1/S_0 CI.

The steepness of this path indicates an ultrafast (on the femtosecond time scale) relaxation. The energy released by the proton transfer in the CT excited state is ca. 58 kcal/mol. The S_1/S_0 CI reached by proton transfer in the CT state leads to backward electron transfer, as is confirmed by the analysis of

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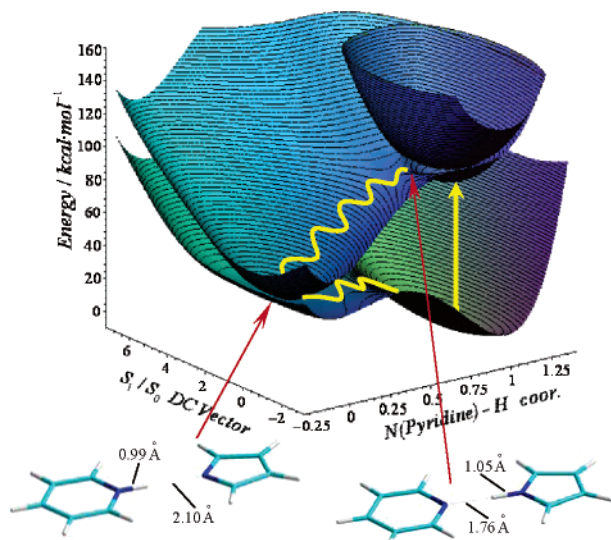**Figure 1.** Perspective view of the PESs (S_2, S_1, and S_0) involved in the radiationless deactivation of the lowest $^1\pi\pi^*$ excited state of pyrrole−pyridine. The S_2/S_1 and S_1/S_0 crossings are indicated as well as their corresponding molecular structures. Illustrative classical paths (in yellow) indicate the Franck−Condon excitation (arrow), and the relaxation on the S_1 and S_0 surfaces, restoring the initial ground-state configuration. The N(pyridine)−H coordinate is 0 for the S_1/S_0 CI and 1 for minimum on S_0. For the sake of clarity, the coupling at the S_2/S_1 crossing is exaggerated.
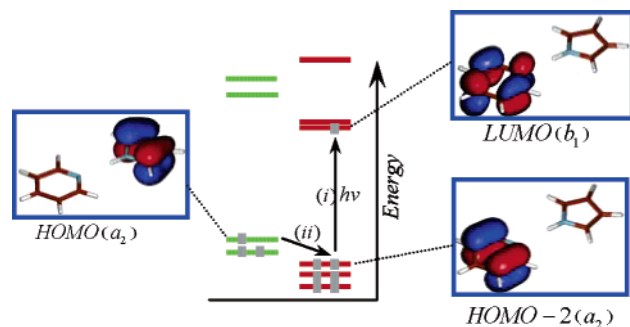

Figure 2. Molecular orbitals involved in the excitation and electron-transfer processes of the pyrrole−pyridine system. The electron-transfer process is composed of two consecutive steps: (i) optical ($h\nu$) excitation of pyridine molecule and (ii) electron transfer from the HOMO of the system (pyrrole) to the hole generated in pyridine (HOMO-2) by optical excitation. Red and green lines indicate pyridine and pyrrole localized MOs, respectively.

Figure 3. (a) DC and GD vectors for the S_1/S_0 CI (note the large contribution of H-transfer motion to the GD vector). (b) Energy of S_1 and S_0 states and (c) charge distribution for S_0 along a loop generated around the S_1/S_0 CI (radius, 0.05 Å). Mulliken charges for S_0 are determined by removing the constant charge of the transferring proton (∼0.5 au). Note that for the steepest path the charge on the pyridine molecule is almost zero (neutral).

size of this model system allows the characterization of the electronic PES with accurate ab initio electronic-structure methods which are not feasible at present for the G/C and A/T base pairs. The treatment of the time-dependent nonadiabatic quantum dynamics of nuclear motion may provide useful benchmarks for ab initio molecular-dynamics simulation of the nuclei by classical trajectories.

Supporting Information Available: Details of the model system, minimum energy paths, molecular geometries of principal structures, and complete references of quantum chemistry packages. This material is available free of charge via the Internet at http://pubs.acs.org.

the charge distribution around the CI. Charge is transferred back from pyridine to pyrrole, thus recovering the neutral pyridine molecule (see Figure 3).

Distortions along the GD and DC vectors remove the energy degeneracy and mix both states (the ground state and the CT state), allowing the system to decay to the ground state (see Figure 3a). Therefore, the S_1/S_0 CI provides a channel of ultrafast decay to the ground state, whereby the approximately 64 kcal/mol of energy carried by the mobile proton is converted into vibrational energy in the closed-shell electronic ground state.[12] This vibrational relaxation on the ground state occurs in the direction of the steepest path on S_0 from the CI (see Figure 3b) given by the GD vector, and corresponds with the complete back electron-transfer process from pyridine to pyrrole (see Figure 3c).

In summary, we have found that the pyrrole−pyridine system represents a potential model of the characteristic ultrafast hydrogen-bond photochemistry of DNA base pairs. The reduced
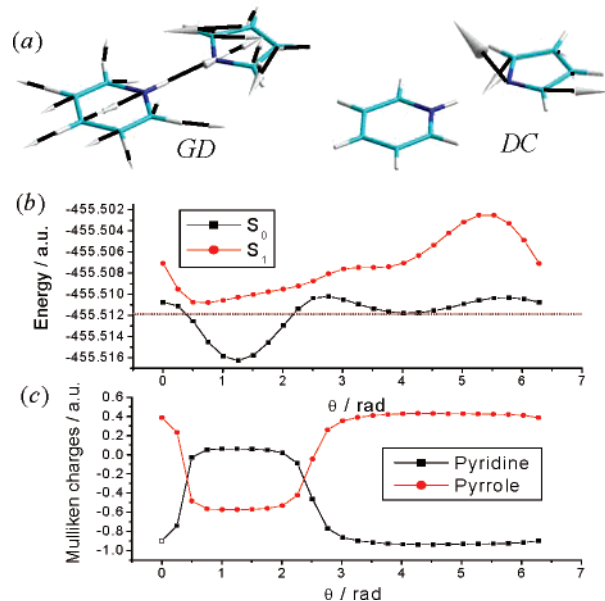
References and Notes

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(5) All calculations were performed at the CASSCF(12,11)/6-31G(d) level of theory, and single-point CASPT2 calculations were performed. Active space was selected to include all π orbitals. CASSCF gradient and frequency calculations were performed with Gaussian 03 (see http://www.gaussian.com/) and CASPT2 single-point calculations with MOLCAS, version 6 (see http://www.teokem.lu.se/molcas/). See the Supporting Information for complete references.

(6) We have focused on the photochemistry of the $^1\pi\pi^*$ state, since it has a higher oscillator strength than the $n\pi^*$ states and is expected to be the more efficiently populated state in DNA base pairs. See: Merchan, M.; Serrano-Andres, L. *J. Am. Chem. Soc.* **2003**, *125*, 8108−8109.

(7) Spectroscopic data were obtained from optimized structures and frequencies at the CASSCF level and single-point calculations at the CASPT2 level. It has to be noted that the $^1\pi\pi^*$ excited state corresponds mainly to pyridine excitation. The energy of this state is in good agreement with previous CASPT2 results for isolated pyridine. See: Lorentzon, J.; Fülscher, M. P.; Roos, B. O. *Theor. Chim. Acta* **1995**, *92*, 67−81.

(8) Since the pyridine and pyrrole moieties are weakly coupled, the π orbitals are localized on either pyridine or pyrrole. The excited states can therefore be classified as locally excited states (on pyridine or pyrrole) or charge-transfer states.

(9) The GD vector gives the molecular distortion of steepest gradient of the energy difference between the adiabatic PESs involved in the crossing, while the DC vector gives the molecular distortion corresponding to the maximum coupling between the states. In the case of the S_2/S_1 AC, the two vectors are parallel (see the Supporting Information for details).

(10) An AC also has been proposed for an intramolecular triplet−triplet energy-transfer process, the mechanism of which is closely related to electron-transfer processes. See: Frutos, L. M.; Sancho, U.; Castaño, O. *J. Phys. Chem. A* **2005**, *109*, 2993−2995.

(11) This value increases to 91 cm^{-1} at the CASPT2 level.

(12) A secondary energy minimum on the ground state corresponding to the proton attached to the pyridine molecule was located. This intermediate is metastable and has an extremely low energy of activation (ca. 1 kcal/mol) for relaxation to the global minimum.