Supplementary data (ESI) for *Physical Chemistry Chemical Physics*

A.L. Sobolewski, *Reversible molecular switch driven by excited-state proton transfer*

Supporting Information

Computational methods

The ground-state equilibrium geometries and the reaction paths of 7-hydroxy-(8-oxazine-2-one)-quinoline (abbreviated as 7HXQ in the following) have been determined with the second-order Moller-Plesset (MP2) method. Excitation energies and response properties have been calculated with the CC2 method [1, 2], which can be considered as the equivalent of MP2 for excited electronic states. The equilibrium geometries and reaction paths of the lowest excited singlet state have been determined at the CC2 level, making use of CC2 analytic gradients [3, 4]. To allow cost-effective explorations of the high-dimensional potential-energy surfaces, the standard split-valence double-zeta basis set of TURBOMOLE [5] with polarization functions on the heavy atoms (def-SV(P)) [6] has been employed in these MP2 and CC2 geometry optimizations.

Three minimum-energy reaction paths have been studied in the ground state and in the lowest excited singlet state of 7HXQ. Two of them involve the transfer of the hydrogen atom from the hydroxyl/azine group of the enol/keto forms 7-hydroxy-quinoline (7HQ) moiety of 7HXQ to the nitrogen atom of the oxazine moiety along the intermolecular hydrogen bond. The OH/NH distance of the hydroxyl/azine group is chosen as the driving coordinate for the hydrogen-transfer reaction path. The system was kept planar along this reaction path (Cs symmetry) and all other nuclear degrees of freedom have been optimized for a given value of the driving coordinate. The third reaction path studied for this system was the twisting of the oxazine moiety with respect to the 7HQ frame. The CCCN dihedral angle was chosen as the driving coordinate for this reaction path. This reaction path was found to lead to a low-lying conical intersection of the S_1 and S_0 PE surfaces near the perpendicular conformation of the two molecular moieties.

Single-point CC2 calculations were performed at the optimized minima of the ground state (vertical absorption spectra) as well along the minimum-energy profiles on the S_0 and S_1 PE surfaces. In these calculations, the cc-pVDZ basis set was used. Additionally, the ground state of the two tautomeric forms of 7HXQ was reoptimized at the DFT/B3-LYP/cc-pVDZ level and the vibrational absorption spectrum was calculated.

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2. C. Hättig and F. Weigend, J. Chem. Phys. 113 (2000) 5154.
3. C. Hättig, J. Chem. Phys. 118 (2003) 7751.
4. A. Köhn and C. Hättig, J. Chem. Phys.119 (2003) 5021.
5. R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, Chem. Phys. Lett. 162 (1989) 165.
6. A. Schaefer, H. Horn and R. Ahlrichs, J. Chem. Phys. 97 (1992) 2571.

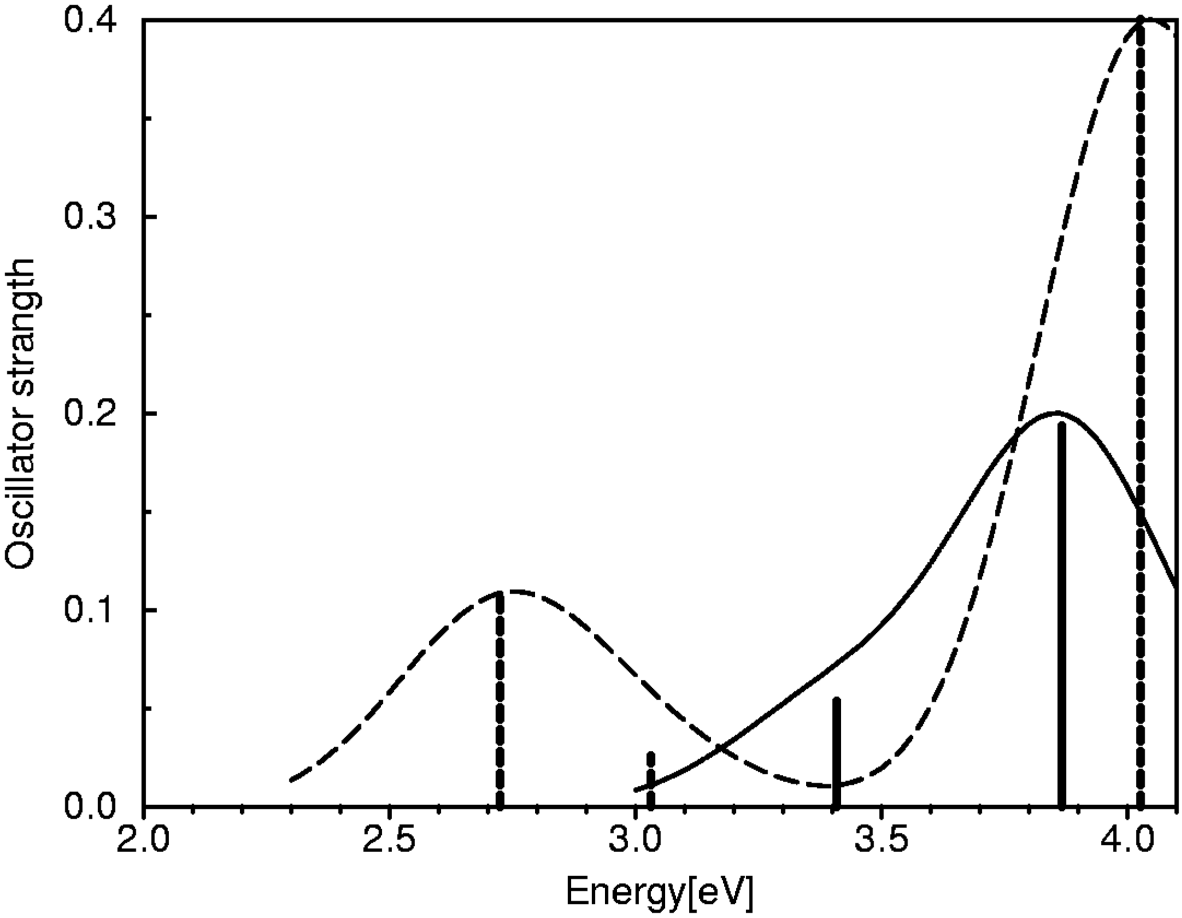

Fig. S1. UV/VIS absorption spectra of the enol (solid sticks) and the keto (dashed sticks) forms of 7HXQ determined with the CC2/cc-pVDZ method at the MP2/def-SV(P) ground-state equilibrium geometry. The spectral envelopes (in arbitrary units) were obtained by convolution of the stick spectra with a Gaussian function of 0.5 eV FWHM.

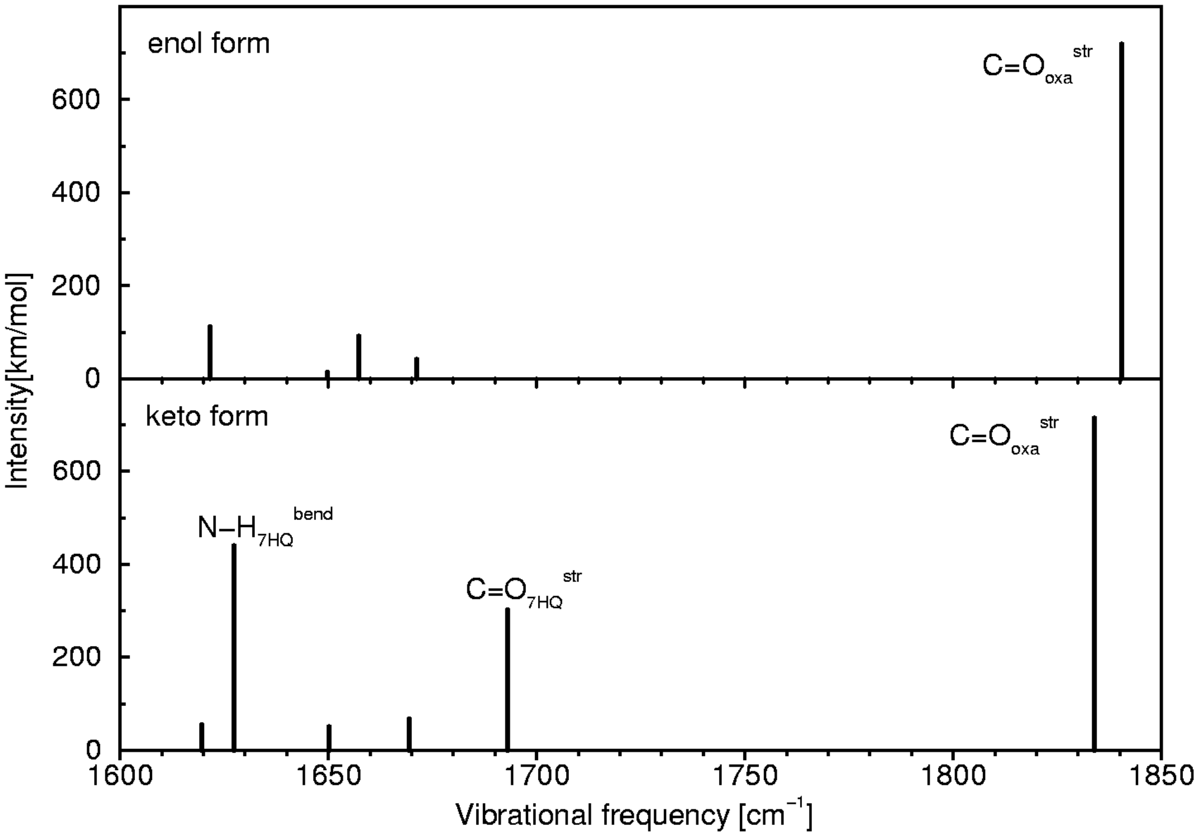

Fig. S2. Part of the IR absorption spectrum of the enol and the keto forms of 7HXQ determined with the DFT/B3-LYP/cc-pVDZ method at the ground-state equilibrium geometry.

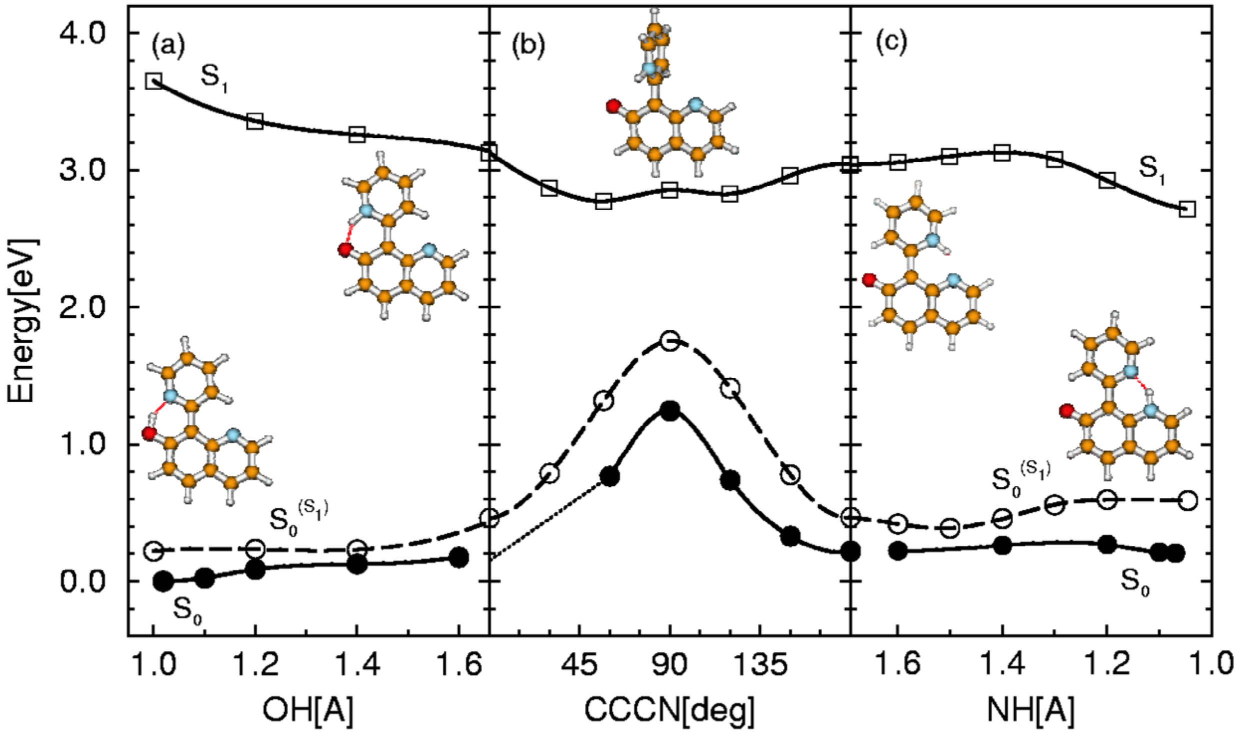

Fig. S3. Energy profiles of 7-hydroxy-(8-pyridyl)-quinoline (7HPQ) in the S_0 state (circles) and in the $^1\pi\pi^*$ state (squares), determined along the CC2/def-SV(P) minimum-energy path (solid curves) for hydrogen transfer from the enol form (a), pyridine-ring torsion (b), and for hydrogen transfer from the keto form (c). $S_0^{(S_1)}$ denotes the energy of the S_0 state, calculated along the minimum-energy path of the $S_1(\pi\pi^*)$ state (dashed curves).