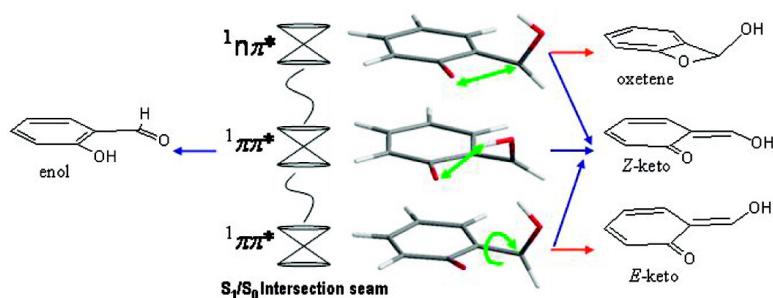## Communication

An Extended Conical Intersection Seam Associated with a Manifold of Decay Paths: Excited-State Intramolecular Proton Transfer in *O*-Hydroxybenzaldehyde

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An Extended Conical Intersection Seam Associated with a Manifold of Decay Paths: Excited-State Intramolecular Proton Transfer in O-Hydroxybenzaldehyde

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O-Hydroxybenzaldehyde (OHBA) is a prototypical photoprotector exhibiting excited-state intramolecular proton transfer (ESIPT).[1] Here we report how its photostability depends on an extended conical intersection seam associated with a manifold of decay paths. Thus, the photoreactivity of OHBA derives from a flat excited-state potential energy surface with barriers of only tenths of electronvolts between the reactant and several conical intersection structures that lead to different products (Scheme 1): two isomers of a hydrogen-bonded intersection (HBI$_{1-2}$) that lead back to the enol reactant or to the tautomerized keto form in its *Z* conformation; an intersection (ZEI) that mediates the *Z*−*E* isomerization of the keto tautomer; and a twisted-pyramidalized one (TPI) that leads to an oxetene adduct. The intersection structures are connected to each other, forming a continuous seam, and the competition between the products depends on where the seam is accessed after the initial excitation. The overall picture must be also valid for the methyl salicylate (MS) and salicylic acid (SA) analogues of OHBA since it reflects the characteristics reported previously for MS[2] and SA.[3]

Femtosecond resolved photoelectron spectroscopy experiments on OHBA find that the proton transfer and internal conversion are decoupled and occur with different time scales.[1] While the proton transfer is complete in approximately 50 fs, the internal conversion rate is temperature and excitation wavelength dependent, with time constants of several picoseconds.[1,4] Experiments on an OHBA analogue with a locked C_2−C_7 bond suggest that the internal conversion depends on out-of-plane modes.[5] Consistent with this, previous calculations on OHBA,[6,7] MS,[2] and SA[3] predict a barrierless planar proton transfer coordinate on the $^1\pi\pi^*$ state, and that the degeneracy for radiationless $S_1{\rightarrow}S_0$ decay is reached along twisting and pyramidalization modes.[2,3] While these studies report the optimization of some conical intersection structures, here we provide a complete picture of the excited-state potential energy surface for OHBA that illustrates the competition between the different decay paths. Thus, the ground- and excited-state potential energy surfaces have been characterized with CASSCF (complete active space self-consistent field) optimizations of critical points (minima, transition structures, and conical intersections) and reaction path calculations[8] based on intrinsic reaction coordinate methodology to connect the minima on S_1 and the intersections. The latter have also been connected to the ground-state products with reaction path calculations. The energies are re-evaluated at the CASPT2 level (complete active space second order perturbation). In general, an active space of 14 electrons in 12 orbitals (OH σ/σ^*, O lone pair, and 9 π) and the 6-31G* basis have been used. The CASSCF calculations have been done with Gaussian03[9] and the CASPT2

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Scheme 1
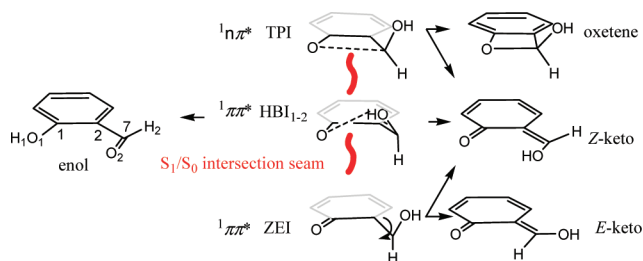
calculations with Molcas5.4.[10] More computational details are given as Supporting Information (SI).

After excitation, the hydrogen transfer on the $^1\pi\pi^*$ state is barrierless and leads from the Franck−Condon (FC) structure to the keto tautomer, K-$^1\pi\pi^*$, a planar minimum with a strong hydrogen bond (O$_1$−H$_1$ bond = 1.61 Å) that lies 0.9 eV below the vertical S_1 excitation. At the FC structure, a $^1n\pi^*$ state is virtually degenerate with the $^1\pi\pi^*$ state, with a calculated gap of less than 0.1 eV (see SI). It has been suggested that crossing to the $^1n\pi^*$ state near the FC region could lower the efficiency of the hydrogen transfer,[7] but this has not been considered here further.

K-$^1\pi\pi^*$ is the hub of the manifold of decay paths. It is the short-lived intermediate detected spectroscopically, and the calculated absorption and emission maxima of 4.1 and 2.1 eV agree well with the experimental values in the gas phase and nonpolar solvents (3.7−3.9 and 2.4−2.5 eV, respectively).[1,4,11] There is a second S_1 keto minimum with $^1n\pi^*$ character, K-$^1n\pi^*$, located 0.3 eV above K-$^1\pi\pi^*$. It has a "looser" geometry (O$_1$−H$_1$ bond = 2.04 Å), and the C$_1$−O$_1$ bond is stretched to 1.37 Å. The barrier between the two S_1 minima is 0.4 eV relative to K-$^1\pi\pi^*$. The $^1n\pi^*$ state of the keto tautomer is relevant because the TPI region of the seam is associated with that state.

The competition between the different decay paths is shown in Figure 1, which is a sketch of the surface region formed by the S_1 keto minima and the seam, based on the calculated paths and the mapping of the seam. The coordinate that leads from the minima to the seam is a rotation around the C$_2$−C$_7$ bond. This bond is a double bond in the keto tautomer, and rotation leads to ethylenic type intersections.[12] The second relevant coordinate connects the $^1\pi\pi^*$ and $^1n\pi^*$ excited-state regions. It is a skeletal rearrangement composed mainly of the C$_1$−O$_1$ bond length coordinate.

The favored decay path from K-$^1\pi\pi^*$ is provided by two conical intersections, HBI$_1$ and HBI$_2$. At these structures, the torsional angle around the C$_7$−C$_2$ bond (O$_2$−C$_7$−C$_2$−C$_1$) is 45−55°. The two isomers have the same electronic structure and differ in the pyramidalization at C$_7$ (O$_2$−C$_7$−H$_2$−C$_2$ values reported in Figure
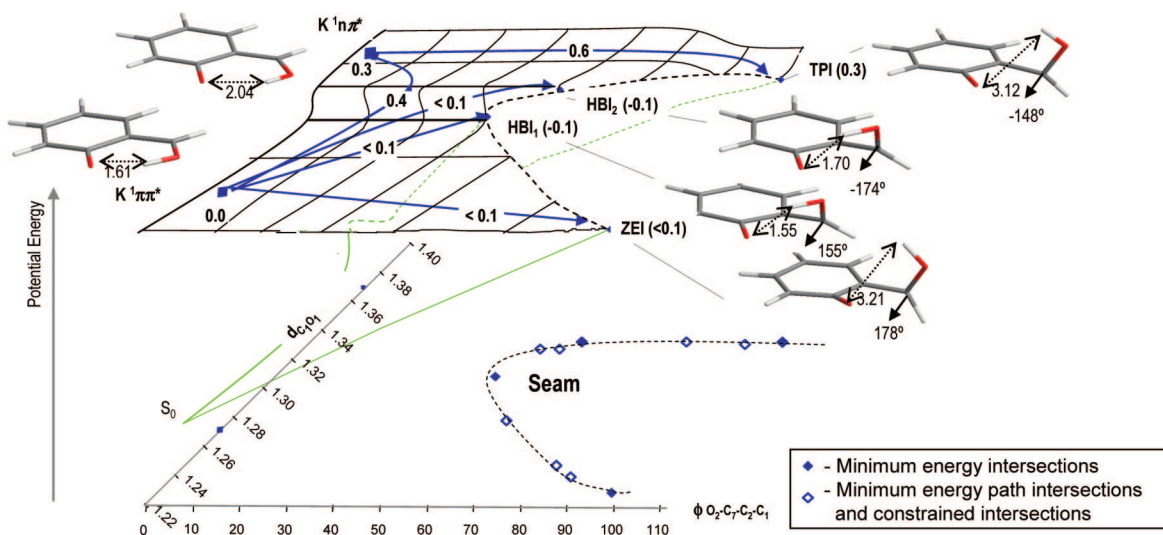
Figure 1. Competing decay paths on the S_1 surface of OHBA. Relative energies of minima, transition structures, and intersections in electronvolts.

1). These structures are analogues of the hydrogen-bonded intersection reported recently for a nitroenamine chromophore that shows ESIPT.[13] This region of the seam explains the photostability of OHBA. Thus, decay at HBI_1 leads directly to the enol reactant, while decay at HBI_2 leads to the Z form of the keto tautomer and proceeds without a barrier to the enol. HBI_1 and HBI_2 can be reached from K-$^1\pi\pi^*$ with small barriers (<0.1 eV), in agreement with the short-lived fluorescence of this minimum.

Decay at the ZEI and TPI regions requires a higher degree of C_2–C_7 rotation, up to approximately 90°, and breaking of the hydrogen bond. Similar structures have been reported for MS,[2] SA,[3] and malonaldehyde (MA).[14] ZEI is separated from K-$^1\pi\pi^*$ by a barrier of less than 0.1 eV.[3] Decay at this region may be photoreactive, as both E and Z isomers of the keto tautomer can be formed and the barrier for thermal $E\rightarrow Z$ isomerization is high (1.84 eV). The alternative decay through TPI involves two activated steps, from K-$^1\pi\pi^*$ to K-$^1n\pi^*$ and from K-$^1n\pi^*$ to TPI, with barriers of 0.4 and 0.3 eV, respectively. Decay at TPI can lead to the Z keto tautomer or to the oxetene product. In the latter case, the reaction would lead to degradation.

The seam segments between HBI_1, ZEI, and TPI have been mapped with conical intersection optimizations constraining the O_2–C_7–C_2–C_1 (HBI_1–ZEI segment) and O_2–C_7–H_2–C_2 (HBI_1–TPI segment) coordinates (see SI). A total of 11 intersection structures have been located, including unconstrained and constrained minima and the minimum energy path intersections (points of intersection found along the K-$^1\pi\pi^*\rightarrow$ZEI and K-$^1n\pi^*\rightarrow$TPI minimum energy paths) (see also Figures SI18–SI20 in SI). To show the connectivity, Figure 1 includes a projection of these structures on the C_1–O_1 and O_2–C_7–C_2–C_1 coordinates. Moving along the seam from ZEI to HBI and TPI, S_1 becomes more $n\pi^*$ in character because of configuration mixing with the close-lying S_2 state (see Figure SI21 in SI). The S_0–S_2 minimal energy separation is 1.2 eV at HBI_2. This suggests that, similar to MA,[14] there is a close-lying three-state intersection. The analysis of this intersection and a better mapping of the seam with intrinsic reaction coordinate calculations in the intersection space[15] will be the subject of future work.

Overall, the HBI and ZEI regions of the seam are separated from the K-$^1\pi\pi^*$ minimum by barriers of less than 0.1 eV. The calculated values are 0.04, 0.05, and 0.07 eV for the barriers to HBI_1, HBI_2, and ZEI, respectively, and are within the accuracy of our CASPT2// CASSCF approach. There is also good agreement with the barriers of 0.1[4] and 0.2 eV[1] fitted to experimental data. The slightly higher experimental barrier could reflect the slowing down of the process by intramolecular vibrational redistribution (IVR) from the skeletal in-plane modes activated during the hydrogen transfer to the out-of-plane twisting modes. Our results also suggest the E keto isomer as a possible photoproduct, although the higher degree of twisting required for the isomerization may disfavor the process, as it requires a larger amount of IVR. The formation of oxetene is less probable because of the higher barrier.

Supporting Information Available: Computational details, Cartesian coordinates, and complete refs 9 and 10.

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