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Supplementary Information: ESIPT in the Pyrrol Pyridine molecule: Mechanism, timescale and yield revealed using dynamics simulations[†]

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CASPT2 active space

Figure S1 presents the active molecular orbitals included in our CASPT2(10e,8o) calculations. It is comprised of the most relevant π and π^* orbitals for the description of the reactive excited state, as well as the σ , σ^* orbitals associated with the N–H bond in the reactant tautomer and the lone pair of the acceptor N atom in order to allow for the description of the bond breaking and bond creation associated with the investigated proton transfer.

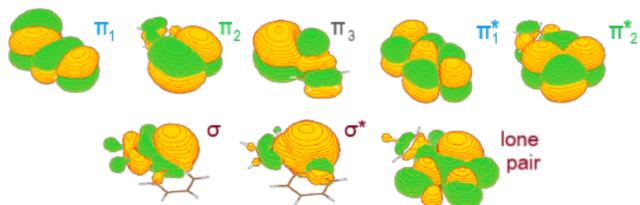


Fig. S1 Representation of the molecular orbitals included in the active space for our CASPT2(10e,8o) calculations.

Static calculations results

We present in Table S1 the results of our static investigation regarding the key points of the PES involved in the ESIPT of PP. These are performed at the CASPT2(10e, 8o) level using the ANO-RCC-VDZP basis-set, see Figure S1 for the active space. We also report for comparison the CC2 and ADC(2) values computed with the def2-SVP basis at the CASPT2 optimized geometries.

ADC(2) and CC2 correctly predict the presence of an activation barrier between reactant and product tautomers on the excited state, although they seem to underestimate its amplitude in comparison to CASPT2. It should be noted, however, that the ADC(2)

Table S1 Relative energy (in eV) of key geometries of the PP molecule. R: Reactant tautomer geometry. P: Product tautomer geometry. TS: Transition state geometry. The numerical indices designate the PES on which the energy is computed (0: ground state ; 1: excited state). The "*" exponent signifies that the geometry optimization was performed on the excited state.

| | R ₁ | R ₁ [*] | Ts ₁ [*] | P ₁ [*] | P ₀ [*] |
|--------|----------------|-----------------------------|------------------------------|-----------------------------|-----------------------------|
| CASPT2 | 4.61 | 4.12 | 4.39 | 2.95 | 0.64 |
| ADC(2) | 4.55 | 4.31 | 4.34 | - | - |
| CC2 | 4.55 | 4.28 | 4.30 | - | - |

and CC2 values reported in Table S1 are obtained at the CASPT2 optimized geometries. It is thus expected that the reported values underestimate the actual amplitude of the activation barrier under these methods.

Distribution of NCCN dihedral angle near degeneracy

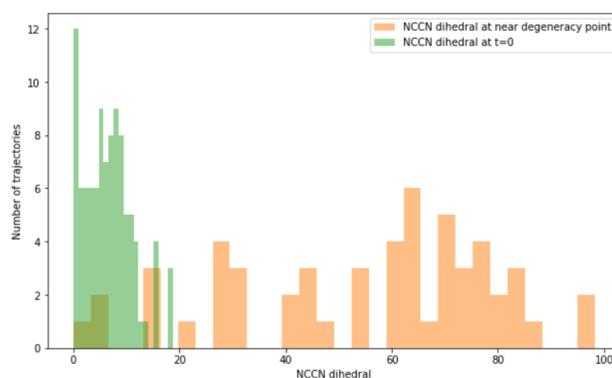


Fig. S2 Distribution of the NCCN dihedral angle at $t = 0$ across our full trajectory set (green) and at the time a given trajectory was considered to have reached a near degeneracy point (orange).

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To characterize the geometry of the molecule at the conical intersection, we report in figure S2 the distribution of the central NCCN dihedral angle at $t = 0$ for all our trajectories and at the time a given trajectory was considered to have reached near degeneracy ($|\Delta E_{S_0, S_1}| < 0.1$ eV). The clear shift toward higher values of the NCCN dihedral distribution at near degeneracy is the signature of the well known twisted conical intersection displayed by this molecule¹. We note that a small number of our trajectories were found to reach near degeneracy while still retaining a very small NCCN dihedral angle. These were found to correspond to geometries displaying significant out of plane distortion of both 5 and 6 atoms rings, potentially indicating the existence of different types of conical intersections.

Time variation of relevant coordinate distributions

Being interested in the proton transfer reaction, we found that it was optimal to represent the position of the proton within an adaptative basis designed to optimally describe the "to be formed" $N^{(2)}-H$ bond of the product tautomer. This basis is internally defined for each molecular geometry by fixing in space the reference plane containing the acceptor nitrogen and its two carbon neighbors in α positions. The $N^{(2)}$ atom is positioned at the origin of the new basis and the proton localization is described by the spherical coordinates $\{\rho, \theta, \phi\}$ (Figure S3). In this representation, ρ represents the distance between the proton and the acceptor nitrogen, θ is the so-called azimuth angle *i.e.* the in plane angle of the proton measured with respect to the bisector of the $CN^{(2)}C$ angle, finally ϕ is the altitude angle of the proton *i.e.* the out of plane angle of the proton with respect to the $CN^{(2)}C$ plane. Being, by construction, intrinsically related to the "to be formed" $N^{(2)}-H$ bond, this basis is expected to accurately capture the specific molecular motion associated with the proton transfer. The time evolution of the distribution of trajectories along these coordinates are shown in Figure S4.

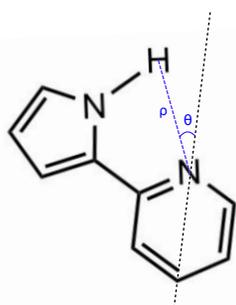


Fig. S3 Representation of internal basis used to characterize the position of the proton with respect to the acceptor nitrogen. We show here the simple planar case where the out of plane angle $\phi = 0$.

References

- 1 M. F. Rode and A. L. Sobolewski, *Chem. Phys.*, 2008, **347**, 413–421.

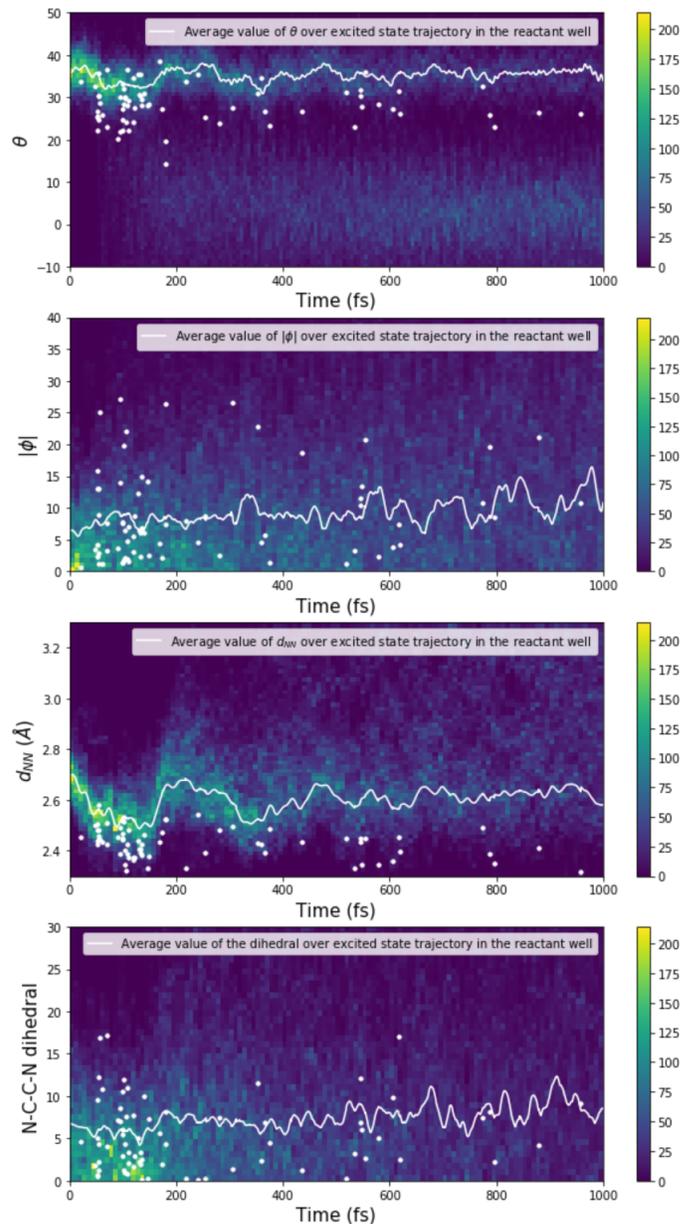


Fig. S4 From top to bottom. Time evolution of the distribution of the θ angle coordinate (azimuth angle associated with the proton in the internal basis representation; see text). Time evolution of the distribution of the absolute value of the ϕ angle coordinate (altitude angle associated with the proton in the internal basis representation). Time evolution of the distribution of d_{NN} (the distance between both nitrogen nuclei). Time evolution of the distribution of the N-C-C-N dihedral angle. All trajectories are included. White line: average value of the coordinate investigated, only taking into account trajectories within the reactant tautomer well on the excited state. White dots: value of the coordinate at each proton transfer time.