# Supporting Information: Nonequilibrium H/D Isotope Effects from Trajectory-based Nonadiabatic Dynamics 

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## Table of Contents

1. Electronic Structure Calculations
2. Dynamics Simulations
3. $\mathrm{S}_{0}$ Minima and Potential Energy Profiles
4. Absorption Spectrum
5. Conical Intersections
6. $S_{1}$ Minimum-Energy Profiles
7. Nonequilibrium H/D Isotope Effects
8. Representative Trajectories
9. Cartesian Coordinates of Optimized Structures

## 1 Electronic Structure Calculations

All semiempirical calculations were performed using the $\mathrm{OM} 2 / \mathrm{MRCI}$ method, $[1-3]$ as implemented in the MNDO99 code. [4] During optimizations, all required energies and gradients were computed analytically. Minimum-energy conical intersections were located using the Lagrange-Newton approach. [5]

The half-electron restricted open-shell Hartree-Fock (HF) formalism [6] was applied in the self-consistent field (SCF) treatment (i.e., the orbitals were optimized for the leading configuration of the $\mathrm{S}_{1}$ state with two singly occupied orbitals). The active space in the multi-reference configuration interaction (MRCI) calculations included 12 electrons in 12 orbitals. In terms of the SCF configuration, it comprised the five highest doubly occupied orbitals, the two singly occupied orbitals, and the five lowest unoccupied orbitals. For the MRCI treatment, three configuration state functions were chosen as references, namely the SCF configuration and the two closed-shell configurations derived therefrom (i.e., all singlet configurations that can be generated from the HOMO and LUMO of the closed-shell ground state). The MRCI wavefunction was built by allowing all single and double excitations from these three references. This semiempirical OM2/MRCI approach has been recently shown to perform well in a comprehensive general evaluation of excited-state properties [7] and in a number of recent excited-state studies. [8-20]

Ground-state geometries were also optimized using density functional theory (DFT) calculations with the hybrid B3LYP exchange-correlation functional [21-23] and the 6-31G* basis set. [24] Vertical excitation energies were calculated at these structures using the linear-response TD-DFT (time-dependent DFT) approach, the B3LYP [21-23] and CAM-B3LYP [25] functionals, and the 6-31++G** basis set. [26]

The parameterized, DFT-based multi-reference configuration interaction (DFT/MRCI) method [27] was also used to calculate the vertical excitation energies. To be consistent with the original parameterization, the hybrid BHLYP functional [23] and the TZVP basis set [28, 29] were employed in the DFT/MRCI calculations.

In addition, the complete-active-space self-consistent field (CASSCF) method was applied to optimize the ground- and excited-state structures and to scan the relevant potential energy profiles. In the CASSCF calculations, an active space of ten electrons in eight orbitals was adopted. The multi-state CASSCF second-order perturbation method (CASPT2) [30] was employed to determine improved single-point energies at all CASSCF structures. The MS-CASPT2 calculations were done using two roots with equal weights and the imaginary shift technique (0.3 a.u.). [31]

The following codes were used for the electronic structure calculations in this work: ChemShell 3.4 [32] and MNDO99 [4] for OM2/MRCI; GAUSSIAN09 [33] for DFT, TD-DFT, and minimum-energy conical intersection optimizations (CASSCF); MOLCAS 7.6 [34, 35] for CASSCF and MS-CASPT2; and TURBOMOLE 5.7.1 [36] for DFT/MRCI. [27]

Table 1: The Number of Trajectories that (a) Undergo ESIPT, (b) Decay to the $\mathrm{S}_{0}$ State, and (c) Remain in the $\mathrm{S}_{1}$ State until the End of the Simulation.

| Temperature (T) | Total | ESIPT | $\mathrm{S}_{0}$ | $\mathrm{~S}_{1}$ | Total | ESIPT | $\mathrm{S}_{0}$ | $\mathrm{~S}_{1}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 7 7PyIn-H |  |  |  |  | 7PyIn-D |  |  |  |
| All | 632 | 626 | 569 | 63 | 735 | 714 | 631 | 104 |  |
| $\mathrm{~T}<275 \mathrm{~K}$ | 219 | 216 | 202 | 17 | 344 | 335 | 300 | 44 |  |
| $275 \mathrm{~K}<\mathrm{T}<325 \mathrm{~K}$ | 251 | 249 | 218 | 33 | 253 | 245 | 217 | 36 |  |
| $\mathrm{~T}>325 \mathrm{~K}$ | 162 | 161 | 149 | 13 | 138 | 134 | 114 | 24 |  |

## 2 Dynamics Simulations

In trajectory surface hopping dynamics, there are two main initial-condition sampling schemes. The first one is Wigner sampling, [37, 38] which generates initial coordinates and velocities based on classical or quantum harmonic vibrational modes. The second one is based on canonical classical molecular dynamics (MD). The canonical distribution is satisfied with the use of thermostat algorithms, such as velocity rescaling [39], the Berendsen thermostat, [40] the Andersen thermostat, [41] the Nose-Hoover thermostat, [42, 43] Nose-Hoover chains, [44] or Langevin dynamics [45]. Here, we adopted the Nose-Hoover chains algorithm (with a chain length of 10) for this purpose. We used the default characteristic time of 0.5 ps for the thermostat and a timestep of 1 fs for nuclear motion.

For both target molecules (7PyIn and the deuterated isotopomer 7PyIn-D), ground-state MD runs were performed at the SCC-DFTB level: [46-48] 7 ps of equilibration dynamics were followed by a 10 ps production run, from which 1000 initial atomic coordinates and velocities were randomly selected. The starting points for the subsequent OM2/MRCI nonadiabatic dynamics runs were chosen from this set on the basis of the computed $\mathrm{S}_{0} \rightarrow \mathrm{~S}_{1}$ transition probabilities. A total of 834 [820] surface-hopping trajectories were run up to 2 ps for 7 Pyln [7PyIn-D], with all relevant energies, gradients, and nonadiabatic coupling vectors being computed on-the-fly as needed. For points with an $S_{1}-S_{0}$ energy gap of less than $10 \mathrm{kcal} / \mathrm{mol}$, the fewest-switches criterion was applied to decide whether to hop. [49,50] The time step was chosen to be 0.1 fs for nuclear motion and 0.0005 fs for electronic propagation. The unitary propagator evaluated at the middle point was used to propagate electronic motion. [51,52] Translational and rotational motions were removed in each step. The empirical decoherence correction ( 0.1 au ) proposed by Granucci et al. was employed. [53] The final evaluations were done for the 632 [735] trajectories (see Table 1) that finished successfully and satisfied our energy continuity criterion (no changes greater than $30 \mathrm{kcal} / \mathrm{mol}$ between any two consecutive MD steps). To analyze the effect of thermal fluctuations on the photodynamics of 7Pyln and 7PyIn-D, the trajectories were apportioned into three temperature windows according to the initial conditions. Further technical details are given in our previous publications. [8-20,51,52] The SCC-DFTB sampling with the Nose-Hoover chains technique was done with ChemShell 3.4 [32] and the nonadiabatic OM2/MRCI dynamics simulations were conducted with MNDO99. [4]

syn

anti

syn-ht

anti-ht

Figure 1: Schematic ground-state geometries optimized in this work. In the $\mathrm{S}_{0}$ state, the syn conformer is most stable. Also shown for syn is the chosen numbering scheme.

Table 2: Selected Geometric Parameters and Relative Energies of the Optimized Structures Obtained from OM2/MRCI, B3LYP and CASSCF

|  | N1-H6 (A) | N5-H6 (A) | C2-C3 (A) | N1-C2-C3-C4 ( ${ }^{\circ}$ ) | Energies (kcal/mol) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| OM2/MRCI |  |  |  |  |  |
| S0-syn | 2.14 | 1.01 | 1.48 | 0.0 | 0.0 |
| S0-anti | 4.10 | 1.01 | 1.49 | 140.3 | 3.0 |
| S0-anti-ht | 1.02 | 4.93 | 1.43 | 179.9 | 49.4 |
| S1-syn | 1.90 | 1.04 | 1.44 | 0.0 | 96.3 |
| B3LYP/6-31G* |  |  |  |  |  |
| S0-syn | 2.09 | 1.01 | 1.48 | 0.0 | 0.0 |
| S0-syn-ht | 1.11 | 1.53 | 1.44 | 0.0 | 17.8 |
| S0-anti | 4.18 | 1.01 | 1.48 | 148.3 | 5.9 |
| S0-anti-ht | 1.01 | 4.92 | 1.43 | 179.8 | 34.4 |
| MS-CASPT2/6-31G*/CASSCF(10,8)/6-31G* |  |  |  |  |  |
| S0-syn | 2.18 | 0.99 | 1.49 | 0.0 | 0.0 |
| S1-syn | 1.91 | 1.01 | 1.43 | 0.0 | 99.9 |

The results from the static electronic structure calculations are of course identical for 7Pyln and 7Pyln-D since the nuclear masses do not enter the electronic Hamiltonian. In the dynamics simulations, the atomic mass of the H6 (D6) atom in 7PyIn (7PyIn-D) was assigned to be 1.008 (2.014) amu. This small mass difference has a remarkable influence on the photodynamics.

## $3 \mathrm{~S}_{0}$ Minima and Potential Energy Profiles

In the ground state there are four possible conformers (see Fig. 1), which are referred to as syn, anti, syn-ht, and anti-ht, respectively. The lowest among them is the syn conformer that is more stable than the anti conformer by $5.9 \mathrm{kcal} / \mathrm{mol}$ at the B3LYP/6-31G* level and $3.0 \mathrm{kcal} / \mathrm{mol}$ at the $\mathrm{OM} 2 / \mathrm{MRCI}$ level (see Table 2 and the right panel of Fig. 2). Hydrogen transfer of H 6 in the syn arrangement yields the syn-ht tautomer. At the B3LYP/6-31G* level, it lies $17.8 \mathrm{kcal} / \mathrm{mol}$ above the syn conformer; a scan of the $\mathrm{S}_{0}$ potential energy profile along the hydrogen transfer shows that syn-ht is metastable and occupies a very shallow potential well (with a lowest harmonic frequency of only $78 \mathrm{~cm}^{-1}$ ). At the OM2/MRCI level, there is no syn-ht minimum: all geometry optimization


Figure 2: B3LYP/6-31G* energy profiles for one-dimensional relaxed minimum-energy paths along the N1-H6 bond length (left) and the N1-C2-C3-C4 dihedral angle (right).
attempts starting from a syn-ht-type structure ended up back at the syn conformer. Finally, the anti-ht conformer is dynamically unimportant because of its very high potential energy, $34.4 \mathrm{kcal} / \mathrm{mol}$ at the B3LYP/6-31G* level and $49.4 \mathrm{kcal} / \mathrm{mol}$ at the $\mathrm{OM} 2 / \mathrm{MRCI}$ level.

## 4 Absorption Spectrum

To investigate the excited states in the Franck-Condon region, the vertical absorption spectrum of the SO -syn conformer was computed at the TD-DFT/6-31++G*//B3LYP/6-31G* level using the B3LYP, CAM-B3LYP, and M06-2X exchange-correlation functionals. The spin-allowed $S_{0} \rightarrow S_{1}$ electronic transition is found to give rise to the strongest absorption band (see Fig. 3). This excited singlet state is of partial charge-transfer character so that the conventional global hybrid functional B3LYP underestimates the excitation energy by ca. 0.5 eV , compared with range-separated (CAM-B3LYP) and modern (M06-2X) functionals. The latter give vertical excitation energies (4.06-4.08 eV) that are close to the values from DFT/MRCI (3.95 eV), and CC2 (4.0 eV), but lower than those from OM2/MRCI ( 4.37 eV ) and MS-CASPT2//CASSCF ( 4.34 eV ).

## 5 Conical Intersections

Conical intersections play a central role in nonadiabatic dynamics simulations. The chosen electronic structure method must therefore be able to describe conical intersections reasonably well.

Table 3 lists selected geometric parameters for conical intersection structures obtained from OM2/MRCI and CASSCF. The SA2-CASSCF/6-31G* optimization yields a twisted structure with an N1-C2-C3-C4 dihedral angle of $68^{\circ}$ and an $\mathrm{N} 5-\mathrm{H} 6$ distance of $2.55 \AA$ that indicates a weak hydrogen bonding interaction. The energy of this structure relative to the ground-state minimum is $84.3 \mathrm{kcal} / \mathrm{mol}$ at the CASSCF level. Single-point MS-


Figure 3: Absorption spectrum (half-width at half height: 0.05 eV ) from CAM-B3LYP/6-31++G**/B3LYP/6-31G* calculations.

Table 3: Selected Geometric Parameters and Relative Energies of the Optimized Conical Intersections Obtained from OM2/MRCI and CASSCF (see text)

|  | N1-H6 $(\AA)$ | N5-H6 $(\AA)$ | C2-C3 $(\AA)$ | N1-C2-C3-C4 $\left({ }^{\circ}\right)$ | Energies (kcal/mol) |
| :--- | :---: | :---: | :---: | :---: | :---: |
| OM2/MRCI |  |  |  |  |  |
| S1S0-MECl-1 | 1.06 | 2.03 | 1.50 | 50.4 | 78.8 |
| S1S0-MECI-2 | 1.05 | 2.15 | 1.49 | 56.6 | 78.8 |
| S1S0-MECI-3 | 1.02 | 2.92 | 1.48 | 67.7 | 82.6 |
| S1SO-MECI-4 | 1.02 | 3.50 | 1.48 | 90.4 | 77.3 |
| CASSCF(10,8)/6-31G ${ }^{*}$ |  |  |  |  |  |
| S1S0-MECI | 1.00 | 2.55 | 1.49 | 63.2 | 84.3 |

CASPT2/6-31G* calculations lead to a splitting of the two degenerate CASSCF states, with energies of 67.0 and $77.6 \mathrm{kcal} / \mathrm{mol}$.

At the OM2/MRCI level, we find that the optimizations converge to conical intersection structures with different $\mathrm{N} 1-\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4$ dihedral angles and $\mathrm{N} 5-\mathrm{H} 6$ distances depending on the $\mathrm{N} 1-\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4$ value in the starting geometry and on the chosen convergence criteria. Table 3 lists four such structures with varying degrees of hydrogen bonding (see N5-H6 distance). Their energies are rather similar ( $77.3-82.6 \mathrm{kcal} / \mathrm{mol}$ ) and lie in the range of the MS-CASPT2/6-31G* and CASSCF/6-31G* values (see above). The lowest-energy species S1S0-MECI-4 has a perpendicular conformation without N5-H6 hydrogen bonding (at $77.3 \mathrm{kcal} / \mathrm{mol}$ ). In the main paper, we refer to this species as the S1S0-MECI from OM2/MRCI.

To summarize, the OM2/MRCI approach yields a rather extended conical intersection region, with similar energies for N1-C2-C3-C4 dihedral angles between $50^{\circ}$ and $90^{\circ}$. The S1S0-MECI obtained from CASSCF is embedded into this region in terms of its structure, and the corresponding CASSCF and MS-CASPT2 singlepoint energies are of similar magnitude as the $\mathrm{OM} 2 / \mathrm{MRCI}$ values.

## $6 \mathrm{~S}_{1}$ Minimum-Energy Profiles

Figs. 4-6 show the minimum-energy profiles along the relevant reaction paths at the MS-CASPT2//CASSCF, CASSCF, and OM2/MRCI levels, respectively, obtained at the optimized $S_{1}$ geometries (full relaxation of all degrees of freedom except for the reaction coordinate). The left panels depict the potential energy profiles for ESIPT using the distance $\mathrm{N} 1-\mathrm{H} 6$ of the forming covalent bond as the reaction coordinate. The shape of these curves is similar at all three levels: the optimized $\mathrm{S}_{1}$ energies stay roughly at a plateau down to an N1-H6 distance of $1.6 \AA$ and then drop as the covalent $\mathrm{N} 1-\mathrm{H} 6$ bond is formed, while the single-point $\mathrm{S}_{0}$ energies go through a maximum at ca. $1.2 \AA$ but always remain below their $S_{1}$ counterparts. In absolute terms, the $S_{1}$ energies are highest for CASSCF, the inclusion of dynamic correlation in CASPT2 causes a downward shift of ca. $10 \mathrm{kcal} / \mathrm{mol}$, and the OM2/MRCI results are still somewhat lower (by ca. $5-10 \mathrm{kcal} / \mathrm{mol}$ ). The right panels of Figs. 4-6 display the $\mathrm{S}_{1}$ and $\mathrm{S}_{0}$ potential energy profiles along the $\mathrm{N} 1-\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4$ dihedral angle, which provide the link to the $\mathrm{S}_{1} / \mathrm{S}_{0}$ conical intersection. On these pathways, the conical intersection is encountered at a N1-C2-C3-C4 dihedral angle of ca. $70^{\circ}$ for CASSCF and ca. $80^{\circ}$ for $\mathrm{OM} 2 / \mathrm{MRCI}$; it becomes an avoided crossing at the MS-CASPT2 level. During the approach to the conical intersection region, the $\mathrm{S}_{1}$ profiles remain rather flat in all cases (with barriers not exceeding $2 \mathrm{kcal} / \mathrm{mol}$ ), while the $\mathrm{S}_{0}$ profiles show a monotonous increase of ca. 15-25 $\mathrm{kcal} / \mathrm{mol}$. Overall, the OM2/MRCI curves are similar enough to their CASSCF and MS-CASPT2 counterparts to support the use of the OM2/MRCI method in the nonadiabatic simulations (see Figs. 4-6).

Finally, we note that analogous energy profiles have been published previously at the CC2/cc-pVDZ level for geometries optimized at MP2/SV(P) $\left(\mathrm{S}_{0}\right)$ and $\mathrm{CC} 2 / \mathrm{SV}(\mathrm{P})\left(\mathrm{S}_{1}\right)$, see Figure 12 of Ref. [54]. The shapes of these profiles are qualitatively similar to those shown here. It should be noted in this context that the $\mathrm{S}_{1}$ energy profile for ESIPT in Ref. [54] seems to drop off significantly faster than those presented here. This is due to the fact that the $\mathrm{S}_{1}$ curve in Ref. [54] refers to a different reaction coordinate, i.e. the distance $\mathrm{N} 5-\mathrm{H} 6$ of the covalent bond being broken (rather than the distance $\mathrm{N} 1-\mathrm{H} 6$ chosen here); we have confirmed that the $\mathrm{OM} 2 / \mathrm{MRCI}$ curve for the $\mathrm{S}_{1}$ ESIPT process also drops off fast when using $\mathrm{N} 5-\mathrm{H} 6$ as reaction coordinate (like in the CC2 case, data not shown).

## 7 Nonequilibrium H/D Isotope Effects

Nonequlibrium H/D isotope effects may occur in chemical reactions when thermodynamic equilibrium is not achieved before the reaction is complete, for example in the case of ultrafast excited-state proton transfer.

From the present dynamics simulations, we can determine the time required for the ESIPT process in each trajectory. We have adopted the geometric criterion to measure the ESIPT time at the point when the distance in the breaking N5-H6 bond exceeds 1.5 A. The corresponding ESIPT time distributions for 7PyIn and 7PyIn-D


Figure 4: MS-CASPT2/6-31G*//SA3-CASSCF $(10,8) / 6-31 \mathrm{G}^{*}$ energy profiles for relaxed one-dimensional minimum-energy paths (MEPs) along the N1-H6 bond length (left) and the N1-C2-C3-C4 dihedral angle (right). The $S_{1}$ MEP is fully optimized with respect to the other coordinates at the CASSF level, while the $S_{0}$ curve is obtained from single-point calculations.


Figure 5: SA3-CASSCF $(10,8) / 6-31 \mathrm{G}^{*}$ energy profiles for relaxed one-dimensional minimum-energy paths (MEPs) along the $\mathrm{N} 1-\mathrm{H} 6$ bond length (left) and the $\mathrm{N} 1-\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4$ dihedral angle (right). The $\mathrm{S}_{1}$ MEP is fully optimized with respect to the other coordinates, while the $\mathrm{S}_{0}$ curve is obtained from single-point calculations.


Figure 6: $\mathrm{OM} 2 / \mathrm{MRCI}$ energy profiles for relaxed one-dimensional minimum-energy paths (MEPs) along the N1H6 bond length (left) and the N1-C2-C3-C4 dihedral angle (right). The $\mathrm{S}_{1}$ MEP is fully optimized with respect to the other coordinates, while the $\mathrm{S}_{0}$ curve is obtained from single-point calculations.


Figure 7: ESIPT time distribution for 7PyIn and 7PyIn-D (see text). The H/D isotope effect shifts this distribution towards longer times.


Figure 8: Time distributions of the $S_{1} \rightarrow S_{0}$ internal conversion for 7PyIn and 7Pyln (D). The H/D isotope effect shifts this distribution towards longer times.
are shown in Fig. 7 along with their average values. These average ESIPT times change by less than 2 fs when applying the alternative criterion that the length of the forming $\mathrm{N} 1-\mathrm{H} 6$ bond drops below $1.1 \AA$. They are consistent with the measured spectroscopic data and isotope effects. Nosenko et al. attributed the first ion signal in their pump-probe REMPI spectra to the ESIPT process and determined its time to be 280 fs in 7 Pyln and 390 fs in 7PyIn-D.[55] Both are close to our estimates of 274 fs [7PyIn] and 339 fs [7PyIn-D], respectively. In addition, we find that the peak of the ESIPT time distribution is shifted by ca. 50 fs when H is replaced by D , from ca. 150 fs ( $\mathrm{H}, 26 \%$ ) to ca. 200 fs ( $\mathrm{D}, 22 \%$ ).

Isotope effects are also seen in the distribution of the $\mathrm{S}_{1} \rightarrow \mathrm{~S}_{0}$ internal conversion time (see Fig. 8). Here the average hopping time is 64 fs longer for 7Pyln-D than for 7Pyln ( 669 fs vs. 605 fs ). This indicates some correlation between the timing of proton transfer and internal conversion, the latter occurring on average about 330 fs after the former (for both isotomers).

The decomposition into different starting temperatures is shown for proton transfer in Fig. 9 and for internal conversion in Fig. 10. The average ESIPT times tend to increase with increasing temperature of the chosen temperature windows (7Pyln from 265 fs to 283 and 281 fs; 7Pyln-D from 301 fs to 381 and 410 fs), which has been rationalized in the main paper by the increased number of nonplanar starting geometries with out-of-plane distortions that are detrimental to the in-plane ESIPT process. The average hopping times seem to inherit this trend of increasing values (7Pyln from 597 fs to 628 and 582 fs; 7PyIn-D from 653 fs to 662 and 722 fs), but to
a lesser extent. The approach to the hopping point in the conical intersection region requires a rotation around the central C2-C3 bond (after ESIPT, see above), which may indeed be facilitated by out-of-plane distortions in the starting geometries that occur at higher temperatures. This may explain the decrease in the average internal conversion time that we find for 7Pyln in the highest temperature window.

## 8 Representative Trajectories

Fig. $11(H)$ and $12(\mathrm{D})$ show the time-dependent evolution of three key geometric parameters, the $\mathrm{S}_{1} / \mathrm{S}_{0}$ nonadiabatic coupling, and the $\mathrm{S}_{1}-\mathrm{S}_{0}$ energy gap during two typical trajectories. Both trajectories sample the same photophysical and photochemical events but at different times.

In the 7Pyln trajectory, the H 6 atom is bound to the N 5 atom for the first 180 fs , with a stable $\mathrm{N} 1 \cdots \mathrm{H} 6-\mathrm{N} 5$ hydrogen bond (see Fig. 11). During this period, the $\mathrm{S}_{1}-\mathrm{S}_{0}$ energy gap is very large (more than $80 \mathrm{kcal} / \mathrm{mol}$ ), the $\mathrm{S}_{1} / \mathrm{S}_{0}$ nonadiabatic coupling is small, and hence the excited-state decay is impossible. The excited-state proton transfer takes place at ca. 180 fs , which immediately yields a planar tautomer (syn-ht) with the N1-H6 . N N5 hydrogen-bond pattern. After roaming in the resulting planar conformation for ca. 200 fs, the N1-C2-C3-C4 dihedral angle starts to twist, and the system then decays to the ground state via an $\mathrm{S}_{1} / \mathrm{S}_{0}$ conical intersection after ca. 800 fs . At this point, the nonadiabatic coupling is much larger (see top-right panel of Fig. 11). After ca. 100 fs of roaming in the $\mathrm{S}_{0}$ state, the H 6 atom returns to N 5 , with quick formation of the syn conformer (see N1-H6 and N5-H6) that triggers internal rotation around the central C2-C3 bond (see N1-C2-C3-C4) and a strong increase in the $\mathrm{S}_{1}-\mathrm{S}_{0}$ energy gap.

Similar dynamical features are observed for the deuterated isotopomer (see Fig. 12), albeit at different times. Here, the proton transfer happens after a much longer roaming period of 800 fs , possibly because of the more "damped" oscillations in the deuterium case (due to the higher mass). The excited-state decay occurs after another 200 fs at around 1000 fs , after some twist around the N1-C2-C3-C4 dihedral angle (see above) that should not be affected much by isotopic substitution. After the conversion to the ground state, the deuterium takes 250 fs for the transfer back to the initial position (syn conformer), which is again much longer than the 100 fs for the parent system. Isotope effects can thus generally be seen at the trajectory level for processes directly involving the H atom being replaced by D .


Figure 9: ESIPT time distributions in three temperature windows of initial conditions (top: less than 275 K ; middle: between 275 and 325 K ; bottom: larger than 325 K ).


Figure 10: Hopping time distributions for the $\mathrm{S}_{1} \rightarrow \mathrm{~S}_{0}$ internal conversion in three temperature windows of initial conditions (top: less than 275 K ; middle: between 275 and 325 K ; bottom: greater than 325 K ).


Figure 11: A typical trajectory for 7PyIn. The excited-state proton transfer and the $\mathrm{S}_{1} \rightarrow \mathrm{~S}_{0}$ internal conversion are completed after ca. 180 fs and after ca. 800 fs, respectively. In the $\mathrm{S}_{0}$ state, the hydrogen atom is transferred back to the original donor atom. See the text for more detail.


Figure 12: A typical trajectory for 7PyIn-D. The excited-state proton transfer and the $\mathrm{S}_{1} \rightarrow \mathrm{~S}_{0}$ internal conversion are completed after ca. 800 fs and after another 200 fs, respectively. In the $S_{0}$ state, the hydrogen atom is transferred back to the original donor atom. See the text for more detail.

## 9 Cartesian Coordinates of All Optimized Structures

### 9.1 DFT structures

| SO-Syn |  |  |  |
| ---: | ---: | ---: | ---: |
|  |  |  |  |
| C | -2.55874 | 0.04229 | 0.00000 |
| C | -1.17352 | -0.30344 | 0.00000 |
| C | -0.13889 | 0.66235 | 0.00000 |
| C | -0.56463 | 1.99877 | 0.00000 |
| C | -1.92143 | 2.35885 | 0.00000 |
| C | -2.92420 | 1.39586 | 0.00000 |
| C | -3.29374 | -1.19093 | 0.00000 |
| C | -2.37086 | -2.20501 | 0.00000 |
| H | 0.16899 | 2.79779 | 0.00000 |
| H | -2.18472 | 3.41293 | 0.00000 |
| H | -3.97164 | 1.68662 | 0.00000 |
| H | -4.36902 | -1.30477 | 0.00000 |
| H | -2.51506 | -3.27672 | 0.00000 |
| C | 1.29051 | 0.27786 | 0.00000 |
| C | 2.33178 | 1.22830 | 0.00000 |
| C | 3.65383 | 0.80466 | 0.00000 |
| H | 2.11163 | 2.28902 | 0.00000 |
| C | 2.85317 | -1.43914 | 0.00000 |
| C | 3.93406 | -0.56290 | 0.00000 |
| H | 4.45847 | 1.53531 | 0.00000 |
| H | 3.01687 | -2.51579 | 0.00000 |
| H | 4.95256 | -0.93793 | 0.00000 |
| N | -1.09925 | -1.67326 | 0.00000 |
| N | 1.57518 | -1.04637 | 0.00000 |
| H | -0.20126 | -2.14128 | 0.00000 |

S0-syn-ht

| C | -2.48414 | 0.54124 | 0.00094 |
| :---: | :---: | :---: | :---: |
| C | -1.16892 | -0.04729 | 0.00157 |
| C | 0.00706 | 0.75288 | 0.00192 |
| C | -0.16358 | 2.15499 | 0.00176 |
| C | -1.43608 | 2.72382 | 0.00114 |
| C | -2.59703 | 1.93020 | 0.00071 |
| C | -3.38196 | -0.57361 | 0.00087 |
| C | -2.58265 | -1.70026 | 0.00113 |
| H | 0.70219 | 2.81101 | 0.00211 |
| H | -1.53099 | 3.80613 | 0.00103 |
| H | -3.57389 | 2.40950 | 0.00029 |
| H | -4.46382 | -0.54406 | 0.00055 |
| H | -2.90158 | -2.73682 | 0.00109 |
| C | 1.29639 | 0.10600 | 0.00241 |
| C | 2.56091 | 0.74030 | 0.00281 |
| C | 3.71934 | -0.01143 | 0.00336 |
| H | 2.61042 | 1.82216 | 0.00268 |
| C | 2.41371 | -2.00978 | 0.00311 |
| C | 3.65846 | -1.42023 | 0.00349 |
| H | 4.68424 | 0.48760 | 0.00367 |
| H | 2.26594 | -3.08469 | 0.00317 |
| H | 4.55520 | -2.02873 | 0.00388 |
| N | -1.23591 | -1.40130 | 0.00162 |
| N | 1.29165 | -1.26489 | 0.00261 |
| H | 0.26923 | -1.69224 | 0.00209 |

SO-anti

| C | -2.01092 | 1.50337 | 1.22617 |
| ---: | ---: | ---: | ---: |
| C | -0.75754 | 0.82682 | 1.22130 |
| C | 0.01453 | 0.67282 | 0.05035 |
| C | -0.53193 | 1.20093 | -1.12387 |
| C | -1.75941 | 1.88331 | -1.13540 |
| C | -2.50061 | 2.04785 | 0.02826 |
| C | -2.52523 | 1.43017 | 2.56655 |
| C | -1.61732 | 0.72644 | 3.30823 |
| H | 0.03016 | 1.07706 | -2.04325 |
| H | -2.12878 | 2.28982 | -2.07287 |
| H | -3.44998 | 2.57699 | 0.01254 |
| H | -3.45630 | 1.84639 | 2.92594 |
| H | -1.63486 | 0.44645 | 4.35245 |
| C | 1.33380 | -0.00360 | 0.02020 |
| C | 2.23062 | 0.06169 | 1.10367 |
| C | 3.45743 | -0.59169 | 1.01708 |
| H | 1.98889 | 0.65818 | 1.97780 |
| C | 2.83615 | -1.27076 | -1.18553 |
| C | 3.77161 | -1.28674 | -0.14904 |
| H | 4.16218 | -0.54489 | 1.84341 |
| H | 3.04864 | -1.78240 | -2.12363 |
| H | 4.71414 | -1.81363 | -0.26202 |
| N | -0.53901 | 0.37900 | 2.51194 |
| N | 1.65329 | -0.65701 | -1.11571 |
| H | 0.18793 | -0.26622 | 2.77838 |

S0-anti-ht

|  | -2.28684 | 1.13175 | 1.32294 |
| ---: | ---: | ---: | ---: |
| C | -0.85850 | 0.80195 | 1.29970 |
| C | -0.17800 | 0.68318 | 0.03570 |
| C | -0.95391 | 0.89967 | -1.14010 |
| C | -2.30177 | 1.21038 | -1.09187 |
| C | -2.97864 | 1.32849 | 0.14201 |
| C | -2.62965 | 1.16820 | 2.70867 |
| C | -1.45829 | 0.87658 | 3.37524 |
| H | -0.50460 | 0.82806 | -2.12979 |
| H | -2.84597 | 1.36585 | -2.01928 |
| H | -4.03894 | 1.57374 | 0.15036 |
| H | -3.60087 | 1.37967 | 3.13711 |
| H | -1.31638 | 0.81063 | 4.44969 |
| C | 1.21325 | 0.36219 | -0.03375 |
| C | 2.04912 | 0.13721 | 1.10014 |
| C | 3.38115 | -0.16705 | 0.94634 |
| H | 1.56472 | 0.22223 | 2.06975 |
| C | 3.16536 | -0.05223 | -1.42522 |
| C | 3.96928 | -0.26783 | -0.34078 |
| H | 3.99369 | -0.33314 | 1.82804 |
| H | 3.50741 | -0.10365 | -2.45244 |
| H | 5.01727 | -0.50674 | -0.47628 |
| N | -0.37793 | 0.65233 | 2.54174 |
| N | 1.84860 | 0.24794 | -1.25429 |
| H | 1.29020 | 0.39864 | -2.08404 |

### 9.2 OM2/MRCI Structures

| SO-Syn |  |  |  |
| ---: | ---: | ---: | ---: |
|  |  |  |  |
| C | -2.54958 | 0.04924 | 0.00000 |
| C | -1.15601 | -0.31744 | 0.00000 |
| C | -0.13675 | 0.66312 | 0.00000 |
| C | -0.55188 | 1.99858 | 0.00000 |
| C | -1.90785 | 2.35267 | 0.00000 |
| C | -2.91643 | 1.39866 | 0.00000 |
| C | -3.29584 | -1.17964 | 0.00000 |
| C | -2.36239 | -2.21322 | 0.00000 |
| H | 0.19343 | 2.80547 | 0.00000 |
| H | -2.17245 | 3.41724 | 0.00000 |
| H | -3.97197 | 1.68715 | 0.00000 |
| H | -4.36863 | -1.27832 | 0.00000 |
| H | -2.56469 | -3.27872 | 0.00000 |
| C | 1.29141 | 0.26992 | 0.00000 |
| C | 2.31671 | 1.23951 | 0.00000 |
| C | 3.64179 | 0.81660 | 0.00000 |
| H | 2.08510 | 2.30651 | 0.00000 |
| C | 2.84235 | -1.44320 | 0.00000 |
| C | 3.91975 | -0.54794 | 0.00000 |
| H | 4.45764 | 1.54794 | 0.00000 |
| H | 3.04761 | -2.53054 | 0.00000 |
| H | 4.94886 | -0.91073 | 0.00000 |
| N | -1.08179 | -1.69425 | 0.00000 |
| N | 1.57165 | -1.04530 | 0.00000 |
| H | -0.21997 | -2.22023 | 0.00000 |

S0-anti

| C | -2.00652 | 1.48573 | 1.22319 |
| ---: | ---: | ---: | ---: |
| C | -0.74022 | 0.80546 | 1.21830 |
| C | 0.01408 | 0.69043 | 0.03535 |
| C | -0.49862 | 1.2092 | -1.12512 |
| C | -1.73211 | 1.93901 | -1.11470 |
| C | -2.48255 | 2.07743 | 0.04594 |
| C | -2.53397 | 1.37168 | 2.55708 |
| C | -1.61282 | 0.63066 | 3.29121 |
| H | 0.07014 | 1.19495 | -2.05608 |
| H | -2.09795 | 2.37929 | -2.04984 |
| H | -3.42420 | 2.63476 | 0.05177 |
| H | -3.46422 | 1.77726 | 2.91598 |
| H | -1.69111 | 0.32856 | 4.33011 |
| C | 1.32379 | -0.00875 | -0.00476 |
| C | 2.24301 | 0.17941 | 1.04551 |
| C | 3.46608 | -0.48190 | 0.98097 |
| H | 2.00883 | 0.83865 | 1.88110 |
| C | 2.76660 | -1.40595 | -1.12379 |
| C | 3.73768 | -1.29707 | -0.11651 |
| H | 4.21050 | -0.35496 | 1.77386 |
| H | 2.97678 | -2.04066 | -2.00322 |
| H | 4.69414 | -1.81510 | -0.20421 |
| N | -0.53244 | 0.29473 | 2.49085 |
| N | 1.59713 | -0.7310 | -1.07232 |
| H | 0.22545 | -0.31106 | 2.76229 |

S0-anti-ht

| C | -2.26721 | 1.12756 | 1.31653 |
| :--- | ---: | ---: | ---: |
| C | -0.82625 | 0.79549 | 1.27164 |
| C | -0.18207 | 0.68507 | -0.00467 |
| C | -0.97438 | 0.90405 | -1.16334 |
| C | -2.31843 | 1.21313 | -1.08301 |
| C | -2.98405 | 1.32894 | 0.15620 |
| C | -2.58166 | 1.15779 | 2.71516 |
| C | -1.39128 | 0.86272 | 3.36542 |
| H | -0.51856 | 0.82992 | -2.16943 |
| H | -2.88836 | 1.37426 | -2.00661 |
| H | -4.05277 | 1.57535 | 0.18120 |
| H | -3.54336 | 1.36693 | 3.15197 |
| H | -1.25963 | 0.79937 | 4.44807 |
| C | 1.20588 | 0.36477 | -0.07105 |
| C | 2.00102 | 0.14650 | 1.10785 |
| C | 3.32833 | -0.15730 | 0.97722 |
| H | 1.49421 | 0.23624 | 2.06599 |
| C | 3.16207 | -0.05019 | -1.42273 |
| C | 3.93469 | -0.26116 | -0.29564 |
| H | 3.94486 | -0.32563 | 1.86569 |
| H | 3.59349 | -0.12189 | -2.42983 |
| H | 4.99168 | -0.50321 | -0.39150 |
| N | -0.33408 | 0.64322 | 2.50313 |
| N | 1.84171 | 0.25201 | -1.28975 |
| H | 1.29392 | 0.40305 | -2.13891 |

S1S0

| C | -2.55664 | 0.12056 | 0.13455 |
| ---: | ---: | ---: | ---: |
| C | -1.16472 | -0.27164 | 0.19207 |
| C | -0.17742 | 0.63449 | -0.19204 |
| C | -0.57133 | 1.90677 | -0.65176 |
| C | -1.91561 | 2.27452 | -0.68642 |
| C | -2.92647 | 1.39335 | -0.29360 |
| C | -3.27552 | -1.04176 | 0.56156 |
| C | -2.26187 | -2.03450 | 0.85166 |
| H | 0.19702 | 2.61978 | -0.96198 |
| H | -2.18429 | 3.27774 | -1.03428 |
| H | -3.97624 | 1.69666 | -0.31129 |
| H | -4.34743 | -1.16551 | 0.63895 |
| H | -2.50136 | -3.03325 | 1.22160 |
| C | 1.25585 | 0.28706 | -0.08672 |
| C | 1.98143 | 0.48480 | 1.08195 |
| C | 3.32449 | 0.09764 | 1.13446 |
| H | 1.49594 | 0.94145 | 1.94723 |
| C | 3.14042 | -0.76853 | -1.12042 |
| C | 3.88973 | -0.54341 | 0.01964 |
| H | 3.91827 | 0.27119 | 2.03079 |
| H | 3.55061 | -1.30224 | -1.98461 |
| H | 4.92853 | -0.88849 | 0.05566 |
| N | -1.04209 | -1.59490 | 0.65273 |
| N | 1.83767 | -0.30976 | -1.19479 |
| H | 1.21510 | -0.74205 | -1.87861 |

S1-syn

| C | -2.55177 | 0.06588 | 0.00000 |
| ---: | ---: | ---: | ---: |
| C | -1.15455 | -0.25759 | 0.00000 |
| C | -0.11746 | 0.69817 | 0.00000 |
| C | -0.58580 | 2.05208 | 0.00000 |
| C | -1.93649 | 2.37081 | 0.00000 |
| C | -2.95447 | 1.40935 | 0.00000 |
| C | -3.24126 | -1.17833 | 0.00000 |
| C | -2.23551 | -2.22425 | 0.00000 |
| H | 0.15513 | 2.85975 | 0.00000 |
| H | -2.22686 | 3.43059 | 0.00000 |
| H | -4.00946 | 1.68479 | 0.00000 |
| H | -4.30991 | -1.35092 | 0.00000 |
| H | -2.43903 | -3.29162 | 0.00000 |
| C | 1.25893 | 0.28454 | 0.00000 |
| C | 2.32335 | 1.23488 | 0.00000 |
| C | 3.62459 | 0.77412 | 0.00000 |
| H | 2.10741 | 2.30692 | 0.00000 |
| C | 2.76969 | -1.47305 | 0.00000 |
| C | 3.87164 | -0.60551 | 0.00000 |
| H | 4.46673 | 1.47860 | 0.00000 |
| H | 2.96183 | -2.56804 | 0.00000 |
| H | 4.89024 | -0.99226 | 0.00000 |
| N | -1.02920 | -1.66205 | 0.00000 |
| N | 1.50931 | -1.06294 | 0.00000 |
| H | -0.08700 | -2.09085 | -0.00000 |
|  |  |  |  |

S1-anti

|  |  |  |  |
| ---: | ---: | ---: | ---: |
| C | -2.00672 | 1.52950 | 1.21323 |
| C | -0.73156 | 0.85956 | 1.25196 |
| C | 0.04404 | 0.64643 | 0.08904 |
| C | -0.56392 | 1.10783 | -1.13587 |
| C | -1.78798 | 1.74882 | -1.16137 |
| C | -2.52590 | 2.01029 | 0.00351 |
| C | -1.57169 | 0.82778 | 2.54425 |
| H | -0.01739 | 0.91415 | -2.06052 |
| H | -2.19760 | 2.07968 | -2.12322 |
| H | -3.47560 | 2.54859 | -0.02579 |
| H | -3.44387 | 1.95605 | 2.89692 |
| H | -1.64740 | 0.64784 | 4.41853 |
| C | 1.33312 | 0.01402 | 0.04353 |
| C | 2.18064 | -0.11674 | 1.18591 |
| C | 3.39466 | -0.76489 | 1.04617 |
| H | 1.91962 | 0.34627 | 2.14335 |
| C | 2.90147 | -1.04173 | -1.29195 |
| C | 3.77004 | -1.26569 | -0.20441 |
| H | 4.06758 | -0.87940 | 1.90669 |
| H | 3.21494 | -1.39973 | -2.29408 |
| H | 4.72560 | -1.77032 | -0.34213 |
| N | -0.53575 | 0.43781 | 2.57538 |
| N | 1.73916 | -0.42820 | -1.18744 |
| H | 0.24809 | -0.12651 | 2.89053 |

S1-syn-ht

|  |  |  |  |
| ---: | ---: | ---: | ---: |
| C | -2.50247 | 0.59379 | 0.00094 |
| C | -0.02815 | -0.06913 | 0.00150 |
| C | -0.15850 | 0.66456 | 0.00187 |
| C | -1.40806 | 2.06361 | 0.00172 |
| C | -2.59689 | 1.99089 | 0.00119 |
| C | -3.46637 | -0.45544 | 0.00077 |
| C | -2.69226 | -1.69697 | 0.00116 |
| H | 0.73948 | 2.69204 | 0.00202 |
| H | -1.43570 | 3.79785 | 0.00111 |
| H | -3.56976 | 2.48793 | 0.00032 |
| H | -4.54514 | -0.37262 | 0.00042 |
| H | -3.16305 | -2.68257 | 0.00111 |
| C | 1.29395 | 0.01008 | 0.00241 |
| C | 2.49000 | 0.72755 | 0.00282 |
| C | 3.71861 | 0.06452 | 0.00337 |
| H | 2.47364 | 1.82407 | 0.00270 |
| C | 2.55294 | -2.04841 | 0.00313 |
| C | 3.73949 | -1.34520 | 0.00353 |
| H | 4.65225 | 0.62528 | 0.00366 |
| H | 2.53491 | -3.14587 | 0.00325 |
| H | 4.69410 | -1.87932 | 0.00396 |
| N | -1.41142 | -1.48363 | 0.00157 |
| N | 1.34951 | -1.37903 | 0.00258 |
| H | 0.48182 | -1.91453 | 0.00215 |

S1-anti-ht

|  |  |  |  |
| ---: | ---: | ---: | ---: |
| C | -2.27812 | 1.13038 | 1.29381 |
| C | -0.87721 | 0.80777 | 1.25638 |
| C | -0.96560 | 0.68879 | 0.02918 |
| C | -2.33325 | 1.22011 | -1.12703 |
| C | -3.01442 | 1.33883 | 0.11899 |
| C | -2.61500 | 1.16354 | 2.67463 |
| C | -1.37196 | 0.85249 | 3.38619 |
| H | -0.50556 | 0.83073 | -2.12278 |
| H | -2.86807 | 1.37564 | -2.02388 |
| H | -4.07810 | 1.58363 | 0.16023 |
| H | -3.57650 | 1.37255 | 3.12403 |
| H | -1.31719 | 0.80397 | 4.47578 |
| C | 1.23778 | 0.35842 | -0.02709 |
| C | 2.02838 | 0.14632 | 1.10281 |
| C | 3.38282 | -0.16525 | 0.96016 |
| H | 1.58706 | 0.22408 | 2.09282 |
| C | 3.16669 | -0.05440 | -1.43883 |
| C | 3.95243 | -0.26383 | -0.32206 |
| H | 4.00117 | -0.33125 | 1.84243 |
| H | 3.57303 | -0.12654 | -2.45481 |
| H | 5.01274 | -0.50619 | -0.44026 |
| N | -0.37527 | 0.64831 | 2.58110 |
| N | 1.83132 | 0.25389 | -1.28423 |
| H | 1.26987 | 0.39157 | -2.11941 |

### 9.3 CASSCF Structures

| S0-syn |  |  |  |
| :---: | :---: | :---: | :---: |
| C | -2.53200 | 0.03920 | 0.00000 |
| C | -1.18041 | -0.31549 | 0.00000 |
| C | -0.13840 | 0.65300 | 0.00000 |
| C | -0.55709 | 1.97540 | 0.00000 |
| C | -1.92132 | 2.34336 | 0.00000 |
| C | -2.90163 | 1.39669 | 0.00000 |
| C | -3.28577 | -1.18303 | 0.00000 |
| C | -2.38428 | -2.18916 | 0.00000 |
| H | 0.16396 | 2.76956 | 0.00000 |
| H | -2.17500 | 3.38826 | 0.00000 |
| H | -3.94022 | 1.67749 | 0.00000 |
| H | -4.35198 | -1.28331 | 0.00000 |
| H | -2.53914 | -3.24851 | 0.00000 |
| C | 1.30160 | 0.27055 | 0.00000 |
| C | 2.33544 | 1.22512 | 0.00000 |
| C | 3.64308 | 0.81590 | 0.00000 |
| H | 2.11402 | 2.27287 | 0.00000 |
| C | 2.86370 | -1.42587 | 0.00000 |
| C | 3.93194 | -0.54768 | 0.00000 |
| H | 4.43572 | 1.54260 | 0.00000 |
| H | 3.02648 | -2.48894 | 0.00000 |
| H | 4.94272 | -0.91027 | 0.00000 |
| N | -1.11863 | -1.67633 | 0.00000 |
| N | 1.58865 | -1.03171 | 0.00000 |
| H | -0.26133 | -2.17667 | 0.00000 |


| S1-Syn |  |  |  |
| :--- | ---: | ---: | ---: |
|  |  |  |  |
| C | -2.56148 | 0.04118 | -0.00000 |
| C | -1.16912 | -0.28549 | 0.00000 |
| C | -0.09237 | 0.70508 | 0.00000 |
| C | -0.56791 | 2.03444 | 0.00000 |
| C | -1.95583 | 2.34066 | 0.00000 |
| C | -2.94553 | 1.37334 | -0.00000 |
| C | -3.26570 | -1.21936 | 0.00000 |
| C | -2.32959 | -2.18113 | 0.00000 |
| H | 0.12291 | 2.85192 | 0.00000 |
| H | -2.24252 | 3.37642 | 0.00000 |
| H | -3.98214 | 1.65553 | -0.00000 |
| H | -4.32670 | -1.35848 | 0.00000 |
| H | -2.42481 | -3.24584 | -0.00000 |
| C | 1.27928 | 0.29322 | 0.00000 |
| C | 2.35210 | 1.22906 | 0.00000 |
| C | 3.66021 | 0.79058 | -0.00000 |
| H | 2.15006 | 2.28424 | 0.00000 |
| C | 2.80342 | -1.44973 | 0.00000 |
| C | 3.89682 | -0.61975 | -0.00000 |
| H | 4.47351 | 1.49296 | -0.00000 |
| H | 2.96369 | -2.51742 | 0.00000 |
| H | 4.89077 | -1.02531 | -0.00000 |
| N | -1.06454 | -1.59433 | 0.00000 |
| N | 1.53295 | -1.07717 | 0.00000 |
| H | -0.13734 | -2.00158 | 0.00000 |

## S1S0

| C | -2.56806 | -0.06206 | 0.05024 |
| :--- | ---: | ---: | ---: |
| C | -1.18894 | -0.37163 | 0.05226 |
| C | -0.21641 | 0.60187 | -0.12555 |
| C | -0.69135 | 1.89244 | -0.33743 |
| C | -2.05518 | 2.22089 | -0.33419 |
| C | -3.01017 | 1.25511 | -0.14163 |
| C | -3.21162 | -1.28415 | 0.26276 |
| C | -2.13556 | -2.26903 | 0.38444 |
| H | 0.02498 | 2.67390 | -0.51042 |
| H | -2.34506 | 3.24208 | -0.49988 |
| H | -4.05777 | 1.49502 | -0.14348 |
| H | -4.26253 | -1.48332 | 0.32061 |
| H | -2.27867 | -3.31961 | 0.55145 |
| C | 1.23353 | 0.29330 | -0.01890 |
| C | 2.04950 | 0.91898 | 0.87402 |
| C | 3.45127 | 0.63312 | 0.92905 |
| H | 1.62275 | 1.64132 | 1.54612 |
| C | 3.10728 | -0.97288 | -0.85060 |
| C | 3.94253 | -0.35614 | 0.03156 |
| H | 4.08865 | 1.11272 | 1.64505 |
| H | 3.44834 | -1.71111 | -1.54998 |
| H | 4.98343 | -0.62565 | 0.03486 |
| N | -0.97537 | -1.75239 | 0.26867 |
| N | 1.74454 | -0.62025 | -0.97694 |
| H | 1.15082 | -1.41576 | -1.09263 |

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