

Supplementary Materials

**Hydrogen detachment in 3-amino-1,2,4-triazole driven by repulsive  $1\pi\sigma^*$  state –  
Electron Localization Function study.**

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## Electron Localization Function (ELF),

first introduced by Becke and Edgecombe,<sup>1</sup> is defined by the formula:

$$\text{ELF} = (1 + \chi_\sigma^2)^{-1} \text{ where } \chi_\sigma = \frac{D_\sigma}{D_\sigma^0}$$

$$D_\sigma^0 = \frac{3}{5} (6\pi^2)^{\frac{2}{3}} \rho_\sigma^{\frac{5}{3}} \text{ where } \rho_\sigma(\mathbf{r}) \text{ is a local value of spin density;}$$

$$D_\sigma = \tau_\sigma - \frac{1}{4} \frac{(\nabla \rho_\sigma)^2}{\rho_\sigma} \text{ where } \tau_\sigma(\mathbf{r}) \text{ is the positive definite kinetic energy density.}$$

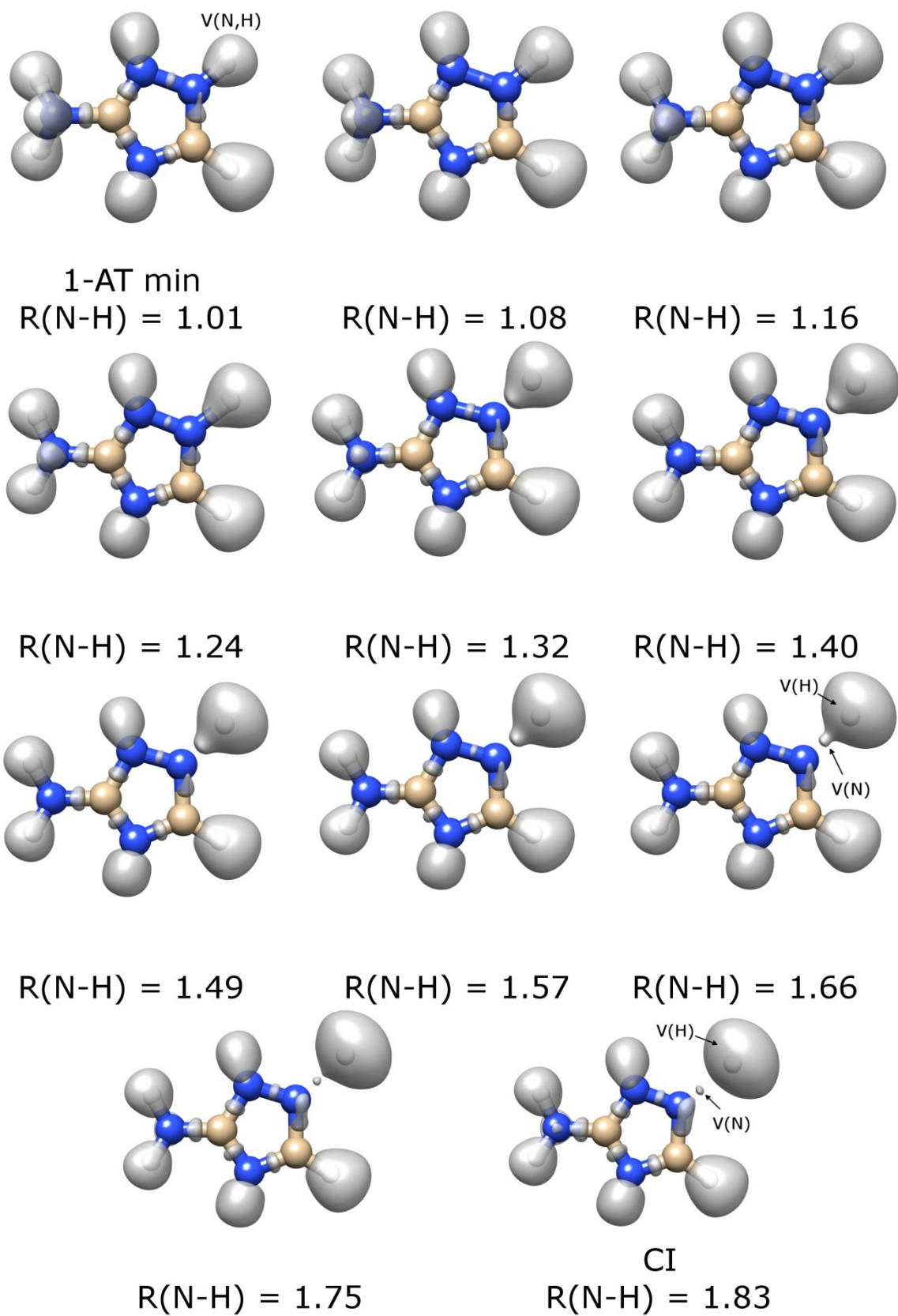
Given the wave function built within the one-particle approximation, the densities can be calculated from orbitals by the formulas for a given spin channel:

$$\rho_\sigma = \sum_i n_i |\varphi_i|^2 ; \tau_\sigma = \sum_i n_i |\nabla \varphi_i|^2 \text{ where } n_i \text{ stands for an occupation number.}$$

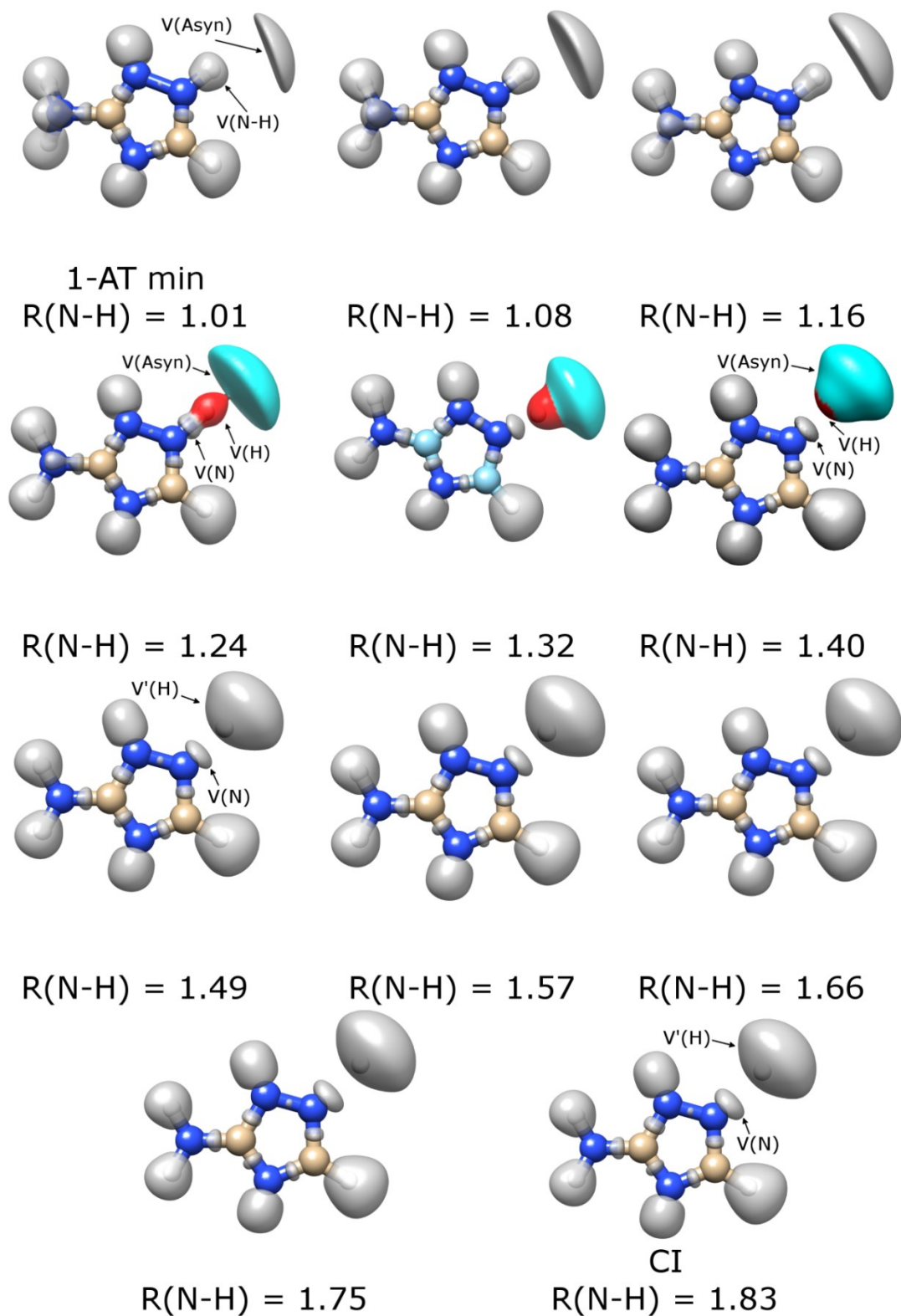
The function was introduced as a tool to measure the probability of same-spin pairing in the real space and by definition its values lie between zero and one, while it reaches its highest values when in the neighborhood of one electron, no other same-spin electron is likely to be found. In the case of Complete Active Space wave function, the orbitals contributing to the densities are the fractionally occupied natural ones onto which the wave function can be projected.

## Complete Active Space Self Consistent Field

Computational cost of CASSCF calculations increase dramatically with the size of the active space. The active space with 8 orbitals and 8 electrons turned out to be sufficient for studying the shape of S0 and <sup>1</sup>πσ\* potential energy surfaces, as reported in our previous paper.<sup>2</sup> In particular, we used CASSCF(8,8) to optimize <sup>1</sup>πσ\*/S0 conical intersection, minima and transition structures on related PESs and to calculate the vibrational spectra to confirm the character of the stationary points. As we discussed in [ref\[2\]](#), the geometrical parameters of stationary structures optimized at CASSCF(8,8)/6-311+g(2d,2p), B3LYP/6-311++g(2d,2p) and B3LYP/aug-cc-pvtz were similar. In present submission we used structures optimized at CASSCF (8,8)/6-311+g(2d,2p) level to compute single point wavefunctions necessary to extract the related electron density and ELF function. The further increase of the active space to 12 orbitals and 12 electrons was due to the fact that for single point energy calculations, which are less computationally demanding than gradients and Hessian, it was feasible to do so, which allowed the further improvement of the quality of the wavefunction. Note, CASSCF is a variational method – the more flexible the active space is the lower the total energy is and the better the wavefunction approximation is. However, the increase of the active space from CASSCF(8,8) to CASSCF(12,12) influenced marginally the obtained results therefore we did not try to extend the active space any further.

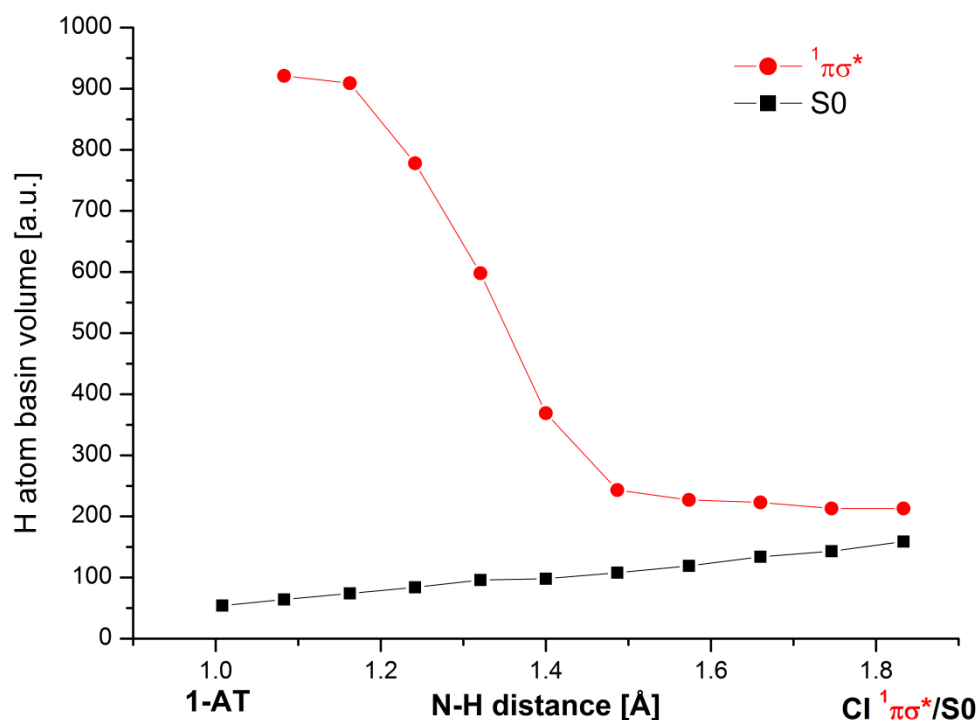


**Figure S1.** 1-AT and related structures along N-H elongation path up to  ${}^1\pi\sigma^*/S0$  conical intersection. Electron localization function using 0.85-localization domains to display relevant basins in  $S0$  state.



**Figure S2.** 1-AT and related structures along N-H elongation path up to  $^1\pi\sigma^*/S_0$  conical intersection. Electron localization function using 0.85-localization domains to display relevant

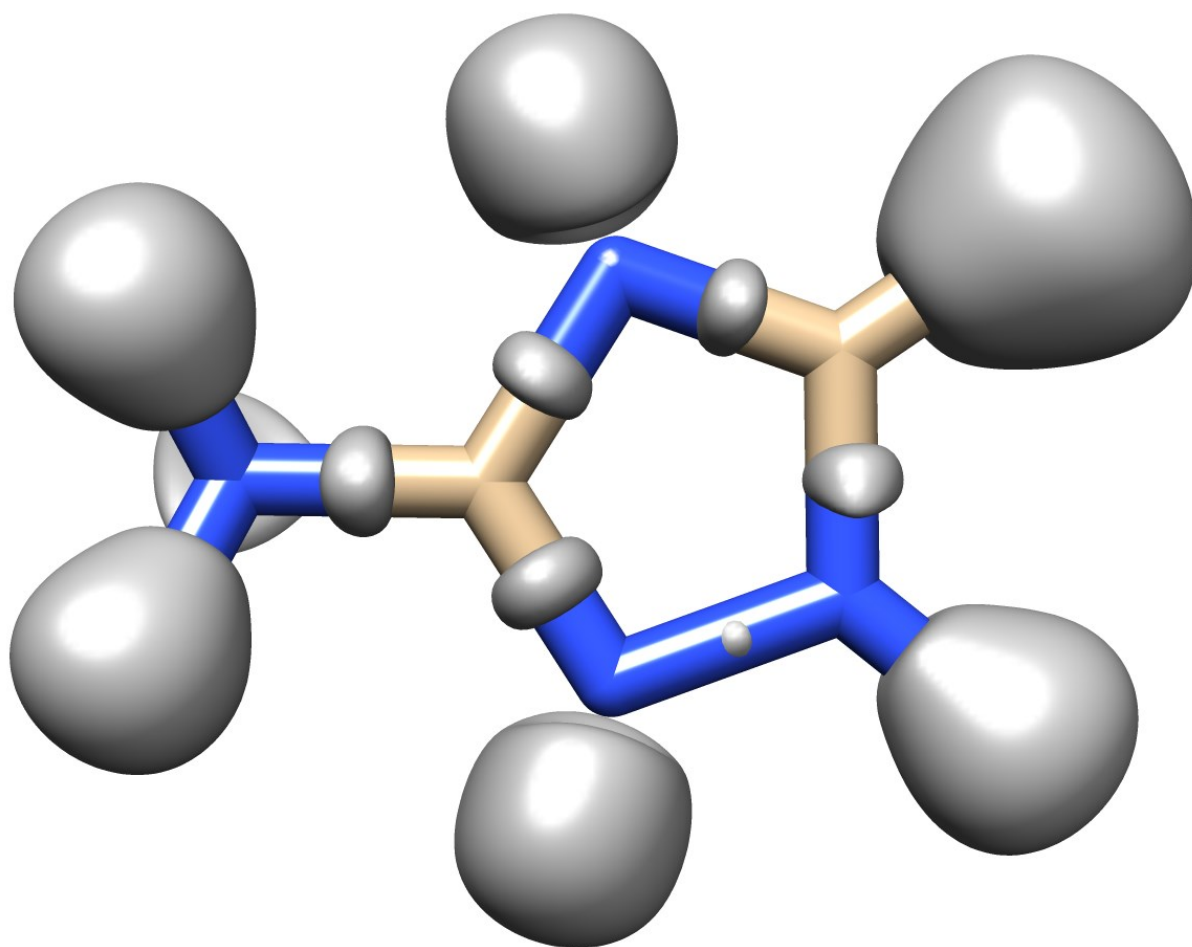
basins in  $^1\pi\sigma^*$  state.  $V(H)$  and  $V(Asyn)$  in the fourth, fifth and sixth structures were singled out by extra colors for clarity.



**Figure S3.** Volume of the topological H atom in S0 and  $^1\pi\sigma^*$  electronic states in 1-AT and related structures along N-H elongation path up to  $^1\pi\sigma^*/S0$  conical intersection.

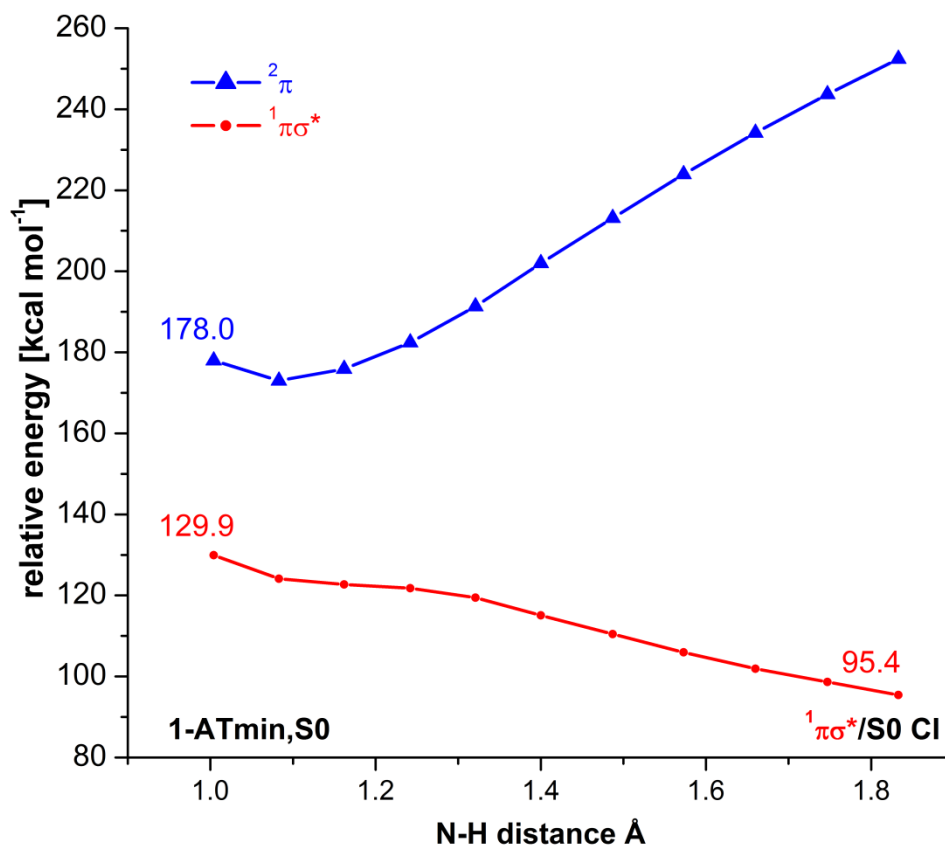
**Comment:** To estimate how the position of the proton in a set of structures varying in N-H distance influence the spatial localization of the electron density pushed outside of the molecule we calculated the volume of the topological H atom defined within Bader's Atoms-in-Molecules theory. The volume of the atom is in this case defined by the separatrix shared with neighboring atoms and by the part of the iso-surface encompassing the whole molecule plotted for arbitrarily chosen low value of the electron density so that the atom (which is in principle an open system) has a finite volume. Defined in such a way the topological hydrogen atom encompasses roughly the space in the proximity of the proton and also the space included in the large asymptotic ELF basin, which allows us to trace the atom volume along the whole N-H dissociation path, irrespective of the details of ELF picture where

relevant  $V(N,H)$ ,  $V(H)$ ,  $V(\text{asyn})$  and  $V'(H)$  basins appear, split or merge on different steps of the process. The volume of the H atom in 1-AT in its ground state is relatively small when the atom is engaged in N-H bond, especially at equilibrium, which suggests that the electron density decays fast with the distance from the proton. In vertically excited 1-AT the electron density diffuses in space, as reflected by multiple increase of the atomic volume. The volume decreases considerably with the elongation of the N-H bond up to  $1.49\text{\AA}$  while further changes of N-H distance influence the volume marginally, which coincides with the bond evolution as revealed by ELF. Namely, up to  $1.24\text{\AA}$  H atom remains covalently bonded to N, then the bond dissociates and the proton dragging some electron density moves towards the asynaptic basin making it more and more compact (the volume of H atom shrinks). Next, at  $R(N-H)=1.49\text{\AA}$  the atom sneaks into the basin, which completes the stage of essential shrinking of the total volume of H atom.



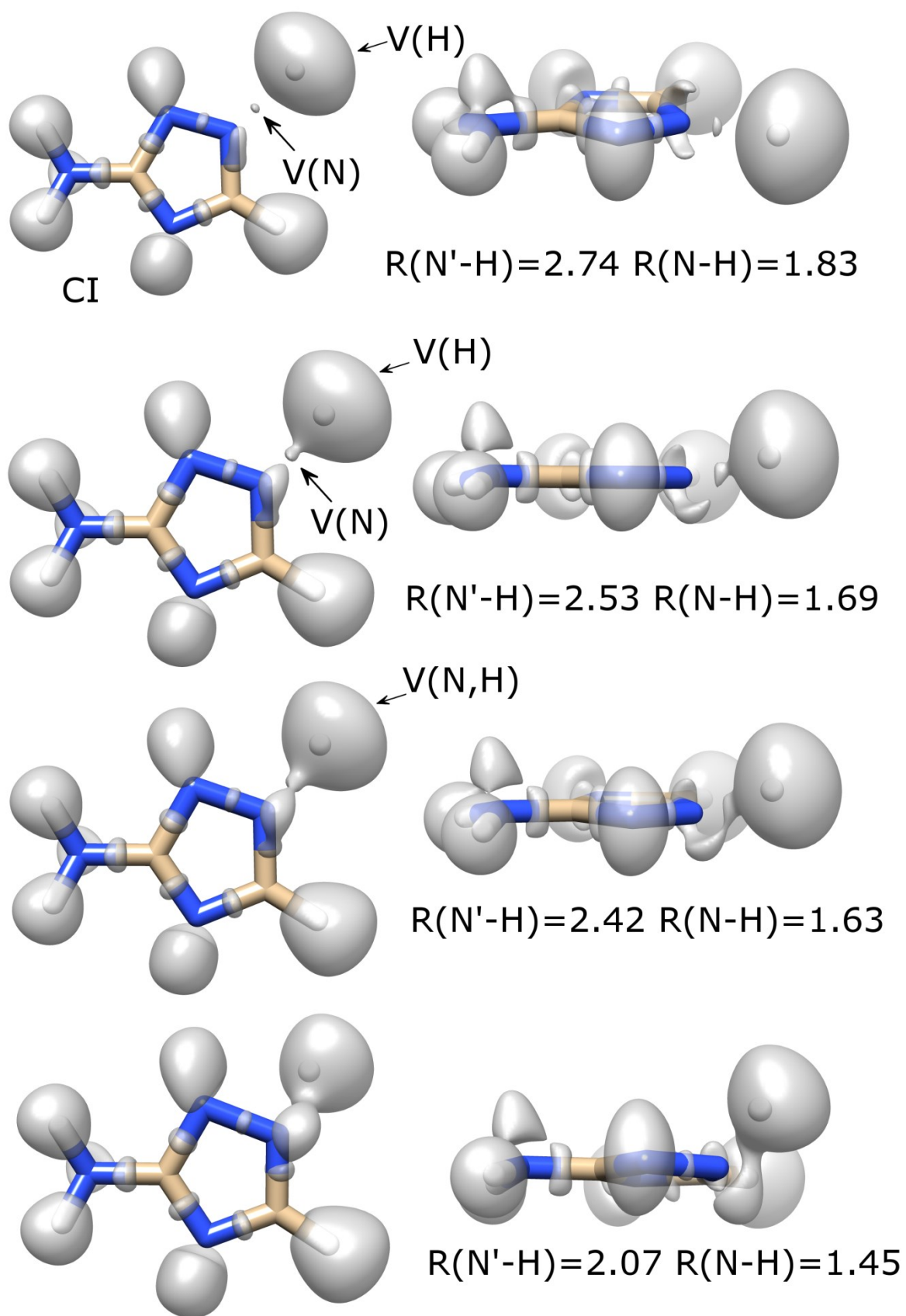
**Figure S4.** Electron localization function using 0.85-localization domains to display relevant basins in  ${}^2\pi$  state for 1-AT structure optimized in  $S_0$  state.

**Comment:** The spatial layout of the basins resembles the one obtained for  $S_0$  state. Clearly, there is no indication of the electron density localized outside the molecule in the vicinity of N-H bond, as was indicated by  $V(\text{Asyn})$  revealed in topology of ELF calculated in  ${}^1\pi\sigma^*$ .

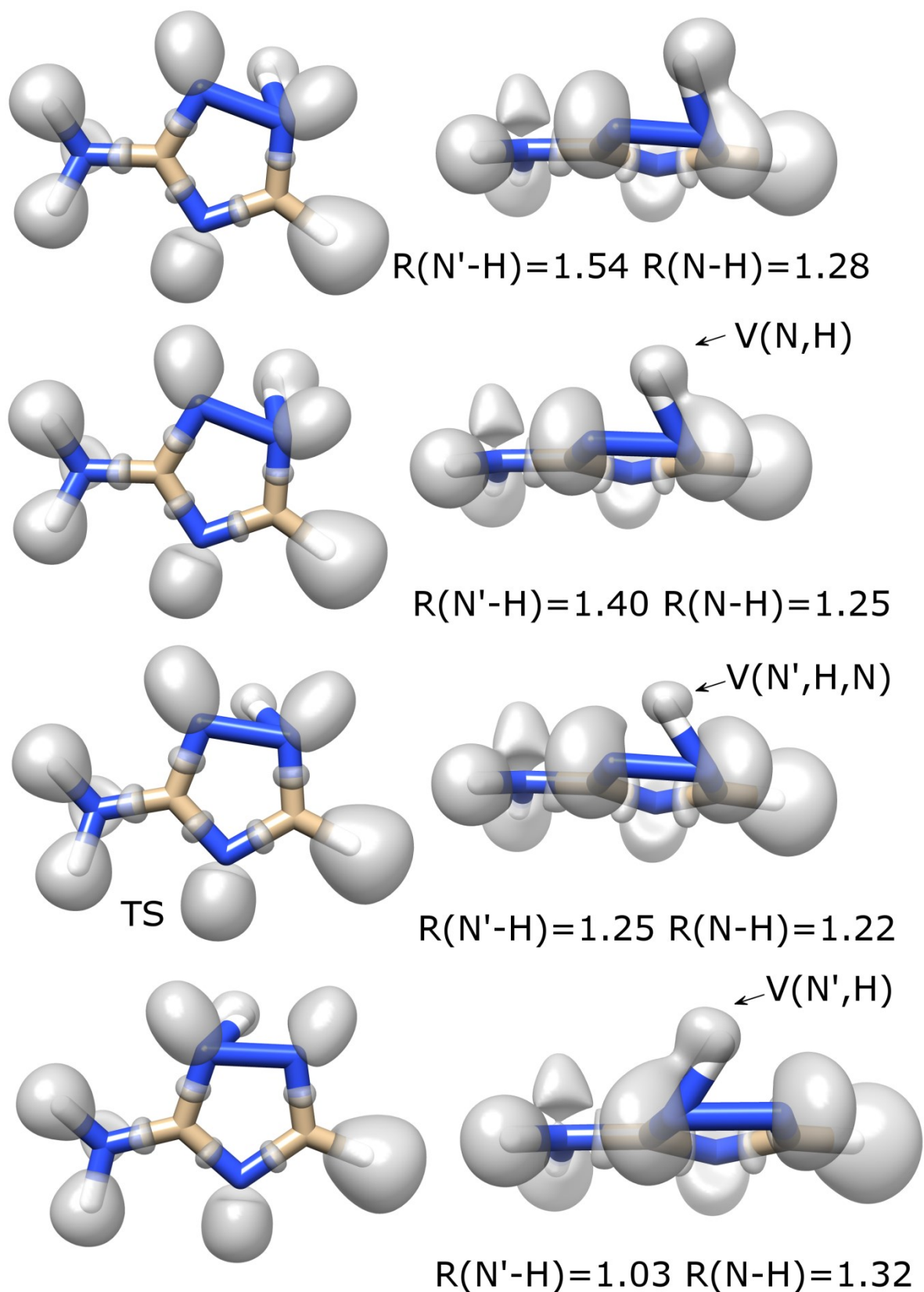


**Figure S5** Relative potential energies along the interpolated path of H atom detachment in neutral 1-AT  $^1\pi\sigma^*$  state and radical cation  $^2\pi$  state. Outermost points represent 1-AT minimum on S0 surface and  $^1\pi\sigma^*/S0$  conical intersection structure, respectively.

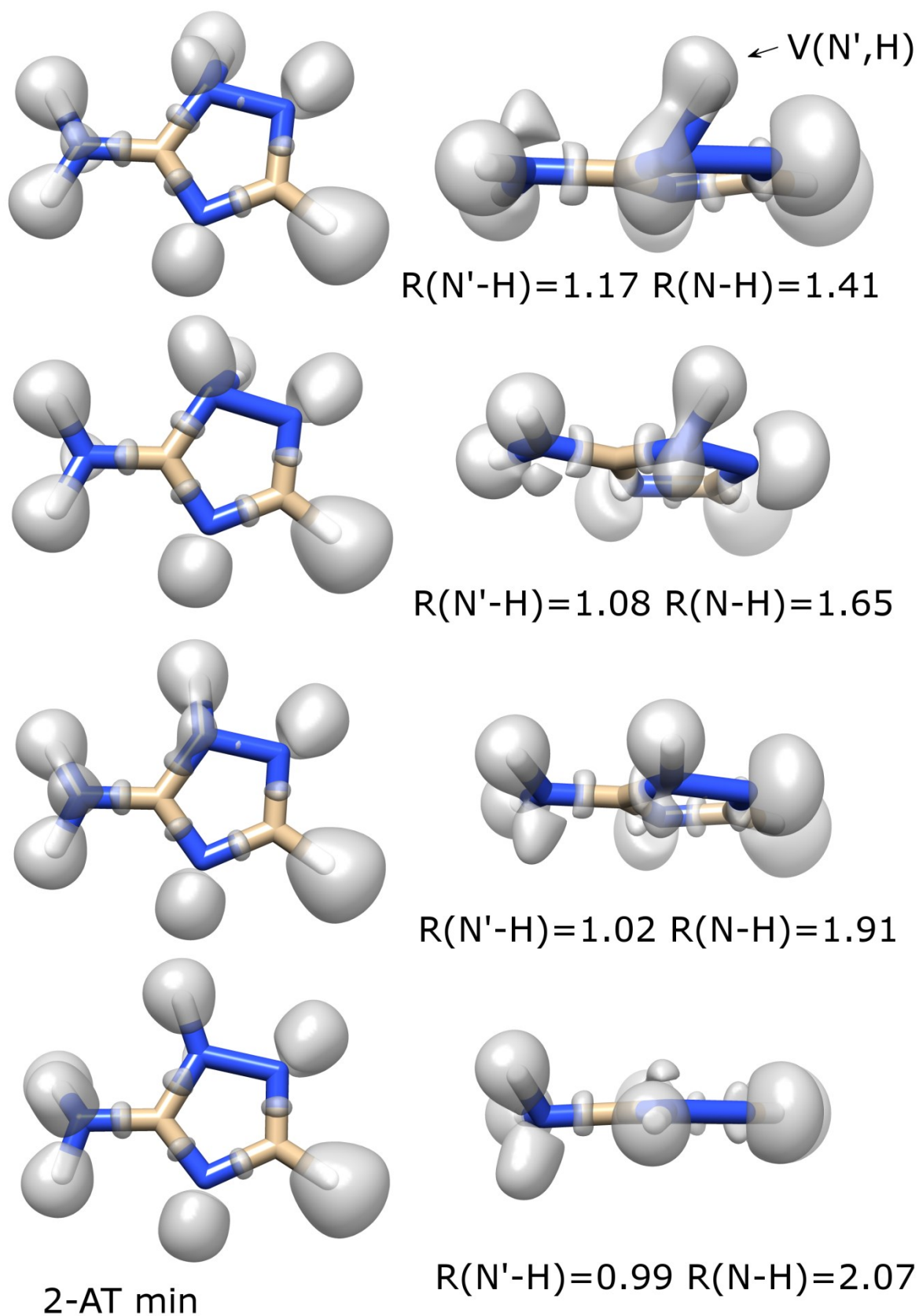




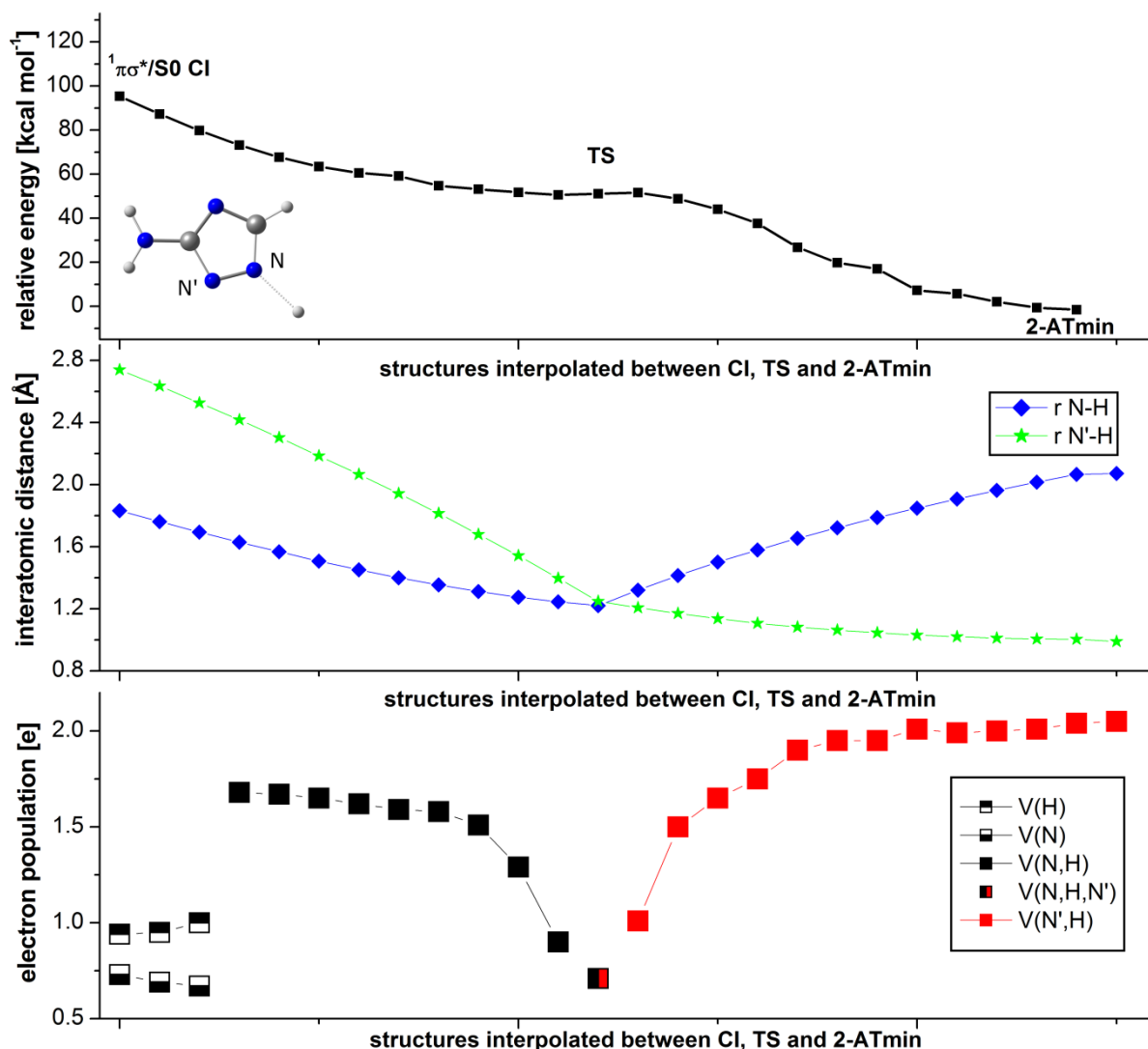
**Figure S6.** Structures linking  $^1\pi\sigma^*/S0$  conical intersection, TS transition structure on  $S0$  and 2-AT minimum. Electron localization function using 0.85-localization domains to display relevant basins in  $S0$  state.



**Figure S7.** Structures linking  ${}^1\pi\sigma^*/S0$  conical intersection, TS transition structure on  $S0$  and 2-AT minimum. Electron localization function using 0.85-localization domains to display relevant basins in  $S0$  state (cont).



**Figure S8.** Structures linking  ${}^1\pi\sigma^*/S_0$  conical intersection, TS transition structure on  $S_0$  and 2-AT minimum. Electron localization function using 0.85-localization domains to display relevant basins in  $S_0$  state (cont).



**Figure S9.** The energy profile and the interatomic distances along the interpolated path linking  $S1(^1\pi\sigma^*)/S0$  conical intersection, TS transition structure on  $S0$  and 2-AT minimum,<sup>2</sup> The electron populations in  $S0$  electronic states of relevant basins of ELF calculated for the structures from the path .

### Comment:

#### The bonds evolution along the second stage of the 1-AT→2-AT hydrogen migration process.

Having crossed the  $S1(^1\pi\sigma^*)/S0$  conical intersection, the further part of the hydrogen atom migration towards 2-AT proceeds along a path on the ground electronic state. Modelling of this process is difficult as CI structure is not a stationary point on the potential energy surface, but rather a hot structure. Moreover, 1-AT molecule excited vertically is reach in kinetic energy while crossing CI point, which cannot be account for in static calculations. However, the important feature of the underlying ground state potential energy surface is the fact that CI structure is located considerably higher in the energy scale that the transition state linking 1-AT and 2-AT minima. Therefore it seems plausible to explore N-H and N'-H bonds

evolution along the path linking optimized CI, TS and 2-AT structures, while the intervening points were linearly interpolated between the optimized ones, which is the approximation to the reaction path applied to study the mechanistic picture of the reaction in the previous paper.<sup>2</sup>

Figures S6-S8 illustrate the evolution of ELF basins engaged in hydrogen atom transfer between N and N' atoms as well as underlying molecular structures along the reaction paths. The energies of the interpolated structures with respect to 1-AT isomer, N-H and N'-H bond distances as well as the electron population of the relevant ELF basins are plotted in Figure S9. At CI structure the H atom lies in plane 1.83Å from N atom and as far as 2.74Å from N' one (Figure S6, Figure S9 central panel). While proceeding towards N' the H atom deviates more and more from the plane up to TS structure in which it is in the shortest distance to both nitrogen attractors ( $R(\text{N-H}) = 1.22\text{\AA}$ ,  $R(\text{N}'\text{-H})=1.25\text{\AA}$ , Figure S7, Figure S9 central panel). Then the atom proceeds further toward N' to form almost planar 2-AT conformer with  $R(\text{N}'\text{-H})=0.99\text{\AA}$  and  $R(\text{N-H})=2.07\text{\AA}$ .

The bond between N and H at CI structure is no longer covalent as at the distance of 1.83Å there are two disjoint basins associated with the atoms populated with 0.73e and 0.94e, respectively (Figure S6, S9). The basins merge to form  $V(\text{N,H})$  basin populated with 1.68e at the interatomic distance of 1.63Å. Although the N-H distance decreases along the few steps of the reaction towards the TS structure, the population of  $V(\text{N,H})$  basin decreases as well due to the puckering of the molecule with H atom considerably protruding from the molecular plane. At the N-H distance of 1.25Å the  $V(\text{N,H})$  basin is populated merely by 0.9e. Simultaneously, the N'-H distance decreases to 1.40Å. TS structure, where N-H and N'-H distances are comparable (ie. 1.22Å and 1.25Å, respectively), coincides with the formation of trisynaptic  $V(\text{N,H,N}')$  basin populated with 0.71e at the expense of the vanishing  $V(\text{N,H})$  one. At this stage of the reaction the alteration of the covalent N-H and N'-H takes place. Further decrease of N'-H distance to 1.03Å (N-H increased to 1.32Å) leads to  $V(\text{N}'\text{H})$  basin populated with 1.01e representing the newly formed covalent bond. Following the further steps of the reaction the hydrogen atom gets less and less protruding from the ring plane, which results in the gain in the  $V(\text{N}'\text{H})$  basin population up to 2.05e in the equilibrium structure of 2-AT, where the N'-H and N-H distances are 0.99Å and 2.07Å respectively.

To sum up, the second step of 1-AT→2-AT tautomerization involves the alteration of N-H and N'-H single covalent bonds, with a proton strongly out of the molecular plane and acting as an attractor for the trisynaptic  $V(\text{N}'\text{H,N})$  basin at TS structure. The structure is not achieved directly from 1-AT minimum along the minimum energy path, but rather from a high energy structure related to the conical intersection linking the first excited state to the ground state.

## References:

- 1 A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.*, 1990, **92**, 5397.
- 2 M. Pagacz-Kostrzewa, A. Bil and M. Wierzejewska, *J. Photochem. Photobiol. A Chem.*, 2017, **335**, 124–129.