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Barrierless Single-Electron-Induced *cis–trans* Isomerization**

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Abstract: *Lowering the activation energy of a chemical reaction is an essential part in controlling chemical reactions. By attaching a single electron, a barrierless path for the cis–trans isomerization of maleonitrile on the anionic surface is formed. The anionic activation can be applied in both reaction directions, yielding the desired isomer. We identify the microscopic mechanism that leads to the formation of the barrierless route for the electron-induced isomerization. The generalization to other chemical reactions is discussed.*

The ability to surpass the energetic barrier between reactants and products is at the very heart of controlling chemical reactions. Various control strategies have been developed over the years that rely, for example, on the use of light, mechanical force, or electric current. Regardless of the chosen external stimulation, the common strategy is either to move the reaction to a different potential energy surface, for example, photochemistry,[1] or to modify the potential energy surface of the reactants, for example, mechanochemistry.[2] Ideally, the target potential energy surface does not only energetically enable the reaction but provides a clear directionality as well.

The idea of activating a chemical reaction by attaching a single electron has been around since the early days of electrochemistry. Still, the prominent role of the electron in many reactions has been restricted to inducing a dissociative electron attachment (DEA) mechanism. The main use of DEA in promoting chemical reactions is through the creation of radicals that continue to react further.[3] Only in the past decade, experiments demonstrating more complicated reactions following electron capture have emerged, for example, multiple bond-breaking,[4] tautomerization,[5] and complex fragmentations.[6] The underlying microscopic mechanism that leads to the electron-driven chemistry in the above examples is still unknown. There have also been a few theoretical works predicting multiple bond-breaking rearrangements following electron attachment.[7]

Herein we demonstrate how the attachment of a single electron can lead to a barrierless *cis–trans* isomerization of maleonitrile (*cis*-1,2-dicyanoethylene, MN) and fumaronitrile (*trans*-1,2-dicyanoethylene, FN). The excess electron transfers the reactants to the anionic potential energy surface (PES) on which there is no longer an energetic barrier towards isomerization. By analyzing the microscopic mechanism responsible for this appealing topology, we gain new insights into the yet unexplored possibilities of electron-driven chemistry.

The *cis–trans* isomerization reaction is one of the most studied reactions with regard to chemical control and chemical switching, for example by light[8] or mechanical force.[9] Very recently it has been shown that the *cis–trans* isomerization rate can be tuned by the presence of a nearby anion.[10]

The isomerization of FN to MN was previously studied using photoinduced electron transfer.[11] In these experiments the FN^- anion is formed in its ground state where an energetic barrier for isomerization is still found, albeit a much smaller barrier.[12] Nevertheless, the isomerization mechanism in these experiments has been shown to proceed through the triplet state of FN which is occupied through electron transfer back to the solvent. Thus in this photochemical isomerization, the ground state of FN^- anion is only temporarily populated and the reaction proceeds on the PES of the triplet state of the neutral FN. As we shall see in the following, a very different situation occurs if the anionic metastable excited state is populated rather than its ground state.

On the ground-state potential energy curve (PEC) of the neutral species, MN displays a high reaction barrier, which corresponds to the formation of a biradical transition state (TS; Figure 1; see the Supporting Information for computational details). The anion of either MN or FN supports only a single electronically stable state. Each of these states, however, belongs to a different irreducible representation. Thus to study the reaction for the anionic species we must follow two different electronic states along the reaction path.

The forthcoming analysis will be more transparent if we use the C_2 point group, which is maintained along the reaction path, rather than the higher point groups of MN and FN. At the equilibrium geometry of MN, the only electronically stable state of the MN^- anion is a $^2A'$ state where the excess electron mostly occupies the lowest π^* orbital. Above the energy of the neutral species, we find a metastable state where the excess electron also occupies the antibonding π space and transforms as the $^2A''$ state. As we shall see in the following, this metastable $^2A''$ state is of special interest for the *cis–trans* isomerization reaction.

Along the reaction path, the energy of the $^2A'$ state rises while the energy of the metastable $^2A''$ state decreases. At an angle of about 60°, the anionic $^2A''$ state crosses the neutral PEC and becomes electronically stable. Continuing further, the two anionic states become degenerate and cross at an angle of 90°. This symmetry allowed crossing is the apex of a conical intersection between the two anionic PESs. As the

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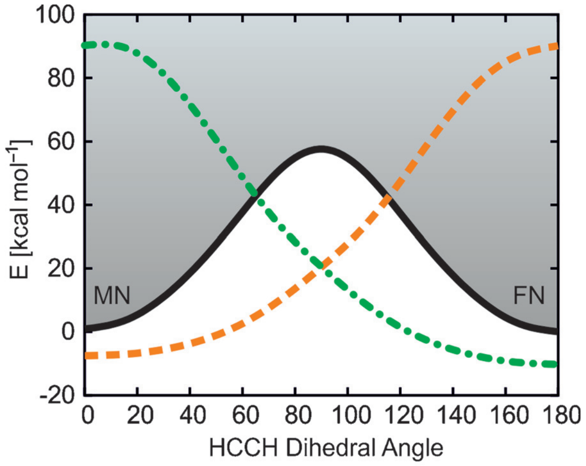

Figure 1. Potential energy curves (PECs) along the *cis–trans* isomerization reaction path of maleonitrile–fumaronitrile (MN–FN) calculated at the multi-reference configuration interaction level.[13] The neutral PEC (black ——) displays a large barrier as expected from the formation of a biradical transition state. For the anion, the lowest PEC in both symmetries is shown: $^2A'$ (orange -----) and $^2A''$ (green –•–•). On the anionic PECs, the reaction starting from the resonance state proceeds without a barrier towards the respective product. At the geometry of the transition state of the neutral species, the two anionic PECs display a conical intersection. The shaded area represents the energetic region where the anion is electronically metastable.

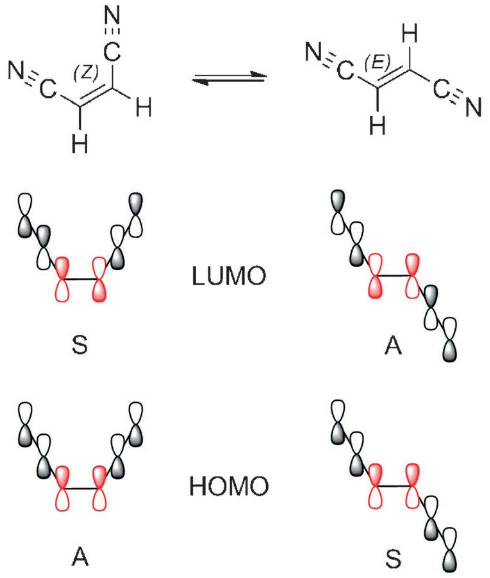

Figure 2. The *cis–trans* isomerization reaction between maleonitrile (left) and fumaronitrile (right). The HOMO and LUMO orbitals of the reactant and the product are also depicted along with their symmetry with respect to the C_2 symmetry axis of each molecule. S or A indicates symmetric or antisymmetric with respect to the C_2 rotation.

geometry of the *trans* product is approached, the previously stable $^2A'$ state crosses the neutral PEC and becomes metastable, whereas the $^2A''$ state becomes the ground state of the FN$^-$ anion. A very similar picture emerges when starting from the FN molecule and following the PECs towards MN while interchanging the roles of the $^2A'$ and $^2A''$ states.

Both of the anionic PECs show no energetic barrier for isomerization. Evidently, starting from MN, if the $^2A''$ anionic resonance were to be populated, the isomerization reaction would proceed in a barrierless fashion. The reverse reaction can also be activated; thus, if for FN the $^2A'$ resonance state were to be populated, the isomerization would be barrierless as well. Even though the reaction on the anionic PEC would be barrierless, two impeding factors must still be dealt with. First, the electronic lifetime of the metastable anionic state needs to be sufficiently long that sufficient population of the anionic state remains by the time the anion becomes electronically stable. Second, the conical intersection of the two anionic surfaces could lead to some leakage back to the original isomer. These two factors will be discussed and mitigated in the following. Nevertheless, the displayed anionic activation seems to be a promising pathway by which complex molecular rearrangements could be induced.

The topology found for the anionic PECs of MN and FN can be understood by examining the underlying anionic wavefunctions. While the above PECs were computed at the multi-reference configuration interaction (MRCI) level, the topology of the PECs is already exhibited by the wavefunctions at a much lower level.

In Figure 2, we show representations of the HOMO and LUMO of MN and FN. The interesting feature that emerges from examining these orbitals is that the HOMO and LUMO interchange their symmetry with respect to the C_2 axis in MN and FN. Furthermore, if the LUMO of MN is rotated to get the FN isomer, the HOMO of FN is not obtained and vice versa. These are the crucial characteristics that lead to the desired topology of the anionic PECs.

The change in symmetry of the HOMO between MN and FN leads to a change in the Hartree–Fock (HF) wavefunction of the two species. In MN, two of the three occupied π orbitals are anti-symmetric with respect to the C_2 axis and one is symmetric, whereas in FN the two occupied are symmetric and there is only one anti-symmetric. As the isomerization reaction proceeds, the two HF configurations mix, leading to the multi-reference character of the biradical. In Figure 3, we

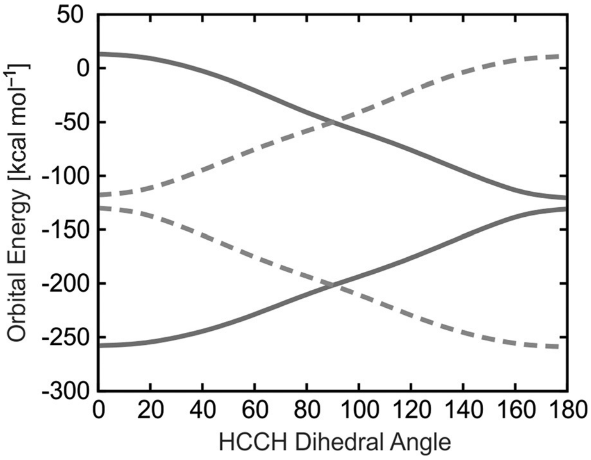

Figure 3. The HOMO and LUMO energies originating from the Hartree–Fock ground state of MN (——) and FN (-----) along the reaction path.

plot the energy of the HOMO along the reaction coordinate for these two configurations (lower solid and dashed lines). As can be seen, the HF ground state switches from one configuration to the other at a dihedral angle of 90°.

When an electron attaches to the LUMO of MN or FN, an anionic state of symmetry ${}^2A'$ and ${}^2A''$, respectively, is formed. Even though from Koopmans' theorem the electron affinities (EAs) of these states are predicted to be negative (see Figure 3), the EAs on the many-body correlated level are positive. Thus these states are correlation-bound anions.[14] For the excited HF wavefunctions of the neutral MN and FN, Koopmans' theorem predicts the anions to be bound. However, the total electronic energy of these two anionic states lie above that of their neutral counterparts (see Figure 1). Thus, the resulting anionic states formed when attaching an electron to the LUMO of the excited configurations are resonance states with a finite lifetime. Since these are Feshbach resonances, that is, the electronic relaxation to the ground state requires the rearrangement of more than one electron,[15] the lifetime of these anionic resonances should be relatively long and we do not expect much of the density to return to the neutral PES before the anion becomes bound along the reaction path. Unfortunately, a more quantitative evaluation of the lifetime of Feshbach resonances for a molecule of this size is still not possible. We note that recent photodetachment experiments have provided evidence for the existence of an electronic resonance in the FN^- anion.[16]

The two anionic PECs (Figure 1) cross at a dihedral angle of 90°. This is a symmetry-allowed crossing of two states of different symmetry, and any displacement along one of the non-totally symmetric modes would lead to the formation of a conical intersection (CI). Since the ground states of FN^- and MN^- anions also have the C_2 point group as a subgroup and the reaction is barrierless along the symmetry-preserving path, we do not expect much losses to the other isomer through the CI. The CI we find in the present reaction is especially interesting since its position is symmetry-dictated.

As the above discussion demonstrates, the topology of the anionic PECs enables the barrierless activation of the isomerization process of MN and FN. Can this topology be expected in other systems and reactions? Our analysis shows that the key points for the anionic PECs to possess such a topology is 1) the ground states of the anionic reactant and anionic product should belong to different irreducible representations under a common point group and 2) there is a path from the reactant to the products in which the joint point group is maintained. These two conditions are hardly unique to isomerization reactions but could rather be found in other chemical reactions as well. Even though we can only predict a priori the existence of such a topology in systems which exhibit some symmetry, there is no reason to exclude asymmetric systems from having PESs with similar structure. Given the above condition and since electronically bound anionic excited states are rather rare,[17] it is relatively safe to assume that if the ground state of the anion of the reactant and product is bound then there will be a Feshbach resonance that could be used to activate the reaction.

The landscape of the PECs of MN^-/FN^- anions further suggests that not only can the neutral isomerization reaction be activated but the anionic species could also be used as a photoswitch. Exact characterization of the photoisomerization reaction requires however further study of the anionic PES. Very recently, photoswitches based on neutral substituted dicyanoethylene have been studied.[18]

In summary, through the use of high-level ab initio methods we have demonstrated the barrierless activation of the MN/FN *cis–trans* isomerization reaction following electron capture. The activation can be achieved in both reaction directions and stems from the existence of a Feshbach-type resonance in the anionic spectrum. The origin of the Feshbach resonance has been traced to the change in the Hartree–Fock configuration along the reaction path that leads to the formation of two anionic states with different symmetry. We suggest that this kind of topology would be found whenever the anionic ground state of the reactant and product belong to different irreducible representations of the same point group that is conserved along the reaction path. This would in turn lead to the possibility to activate many new complex chemical reactions through electron capture.

Keywords: anions · *cis–trans* isomerization · electron-driven reactions · excited states · nitriles

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