Unprecedented Quantum Tunneling Reactions from the Chemistry of 2-Formylphenylnitrenes

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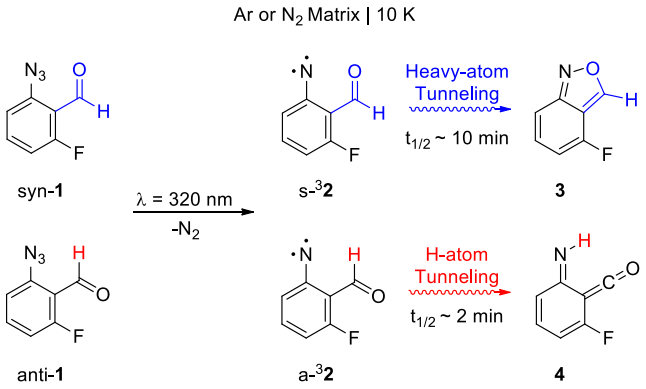
In the early days of quantum mechanics, Bell predicted theoretically that quantum mechanical tunneling (QMT) could contribute significantly to chemical reactions involving the motion of hydrogen atoms.[1] Indeed, reports on the occurrence of H-tunneling are nowadays widespread in the fields of interstellar chemistry, biochemistry and catalysis.[2] Bell also claimed "that all atoms heavier that helium behave, practically speaking, classically". However is nowadays well established that heavy-atom tunneling occurs more often than previously thought.[3]
In 2016, we reported the first occurrence of a tunneling reaction in a nitrene, specifically the [1,4]H-shift reaction of triplet 2-formylphenylnitrene to singlet 6-imino-2,4-cyclohexadien-1-ketene.[4] Since then, we have been using 2-formylphenylnitrene derivatives as targets to study more complex tunneling phenomena. This communication will highlight the most recent discoveries on the chemistry of 2-formyl-3-fluorophenylnitrene. Depending on the aldehyde conformation (**s-**^{3}**2** and **a-**^{3}**2**) and on the matrix-media, the matrix-isolated compound undergoes ring cyclization to benzoxazole **3** or [1,4]H-shift to the corresponding imino-ketene **4**.[5,6] The concepts of spin-forbidden tunneling reactions, conformer-specificity, matrix-medium influence and tunneling control will be discussed from experimental and theoretical standpoints.



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