

CONFORMER-SPECIFIC [1,2]H-TUNNELING IN CAPTODATIVELY-STABILIZED CYANOHYDROXYCARBENE (NC–C–OH)

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We report the gas-phase preparation of cyanohydroxycarbene by high-vacuum flash pyrolysis of ethyl 2-cyano-2-oxoacetate and subsequent trapping of the pyrolysate in an inert argon matrix at 3 K. After irradiation of the matrix with green light for a few seconds singlet *trans*-cyanohydroxycarbene rearranges to its *cis*-conformer. Prolonged irradiation leads to the formation of cyanoformaldehyde and isomeric isocyanoformaldehyde. *Cis*- and *trans*-cyanohydroxycarbene were characterized by matching matrix IR and UV/Vis spectroscopic data with *ab initio* coupled cluster and TD-DFT computations. *Trans*-cyanohydroxycarbene undergoes a conformer-specific [1,2]H-tunneling reaction through a 33.3 kcal/mol barrier (the highest penetrated barrier of all H-tunneling reactions observed to date) to cyanoformaldehyde with a half-life of 23.5 ± 0.5 d; this is the longest half-life reported for an H-tunneling process to date. During the tunneling reaction the *cis*-conformer remains unchanged over the same period of time and the Curtin–Hammett principle does not apply. NIR irradiation of the O–H stretching overtone does not enhance the tunneling rate *via* vibrational activation. Push–pull stabilization of hydroxycarbenes through *s*- and *p*-withdrawing groups therefore is even more stabilizing than push–push substitution.