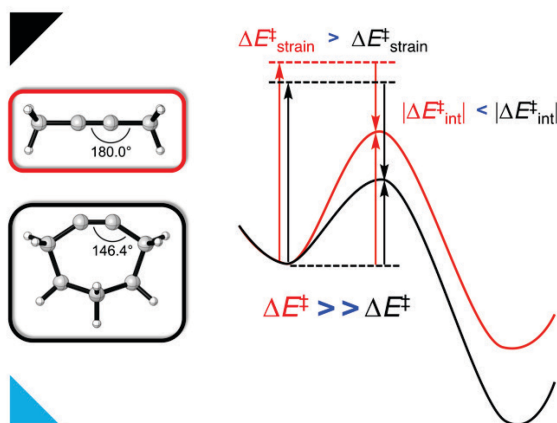


1,3-DIPOLAR CYLOADDITION REACTIVITY OF ALKYNES

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The 1,3-dipolar cycloaddition reactivities of acyclic and cycloalkynes were evaluated using density functional theory (DFT) calculations.^[1] Computed activation free energies for the cycloadditions of the acyclic alkyne (2-butyne) are 16–22 kcal mol⁻¹ higher in energy than for the cyclic alkynes. The strained, or pre-distorted nature of cycloalkynes is often solely used to rationalize this significant rate enhancement. Activation strain and bonding analyses have revealed, for the first time, that the degree of the geometrical pre-distortion of the cycloalkyne ground state geometries acts to enhance reactivity compared to acyclic alkynes via three distinct mechanisms: not only due to (i) a reduced strain energy; but also to (ii) a smaller HOMO–LUMO gap; and (iii) an enhanced orbital overlap, which both contribute to a more stabilizing orbital interactions.

REFERENCES

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