

UNDERSTANDING THE STABILIZING POWER OF σ -ELECTRON DELOCALISATION

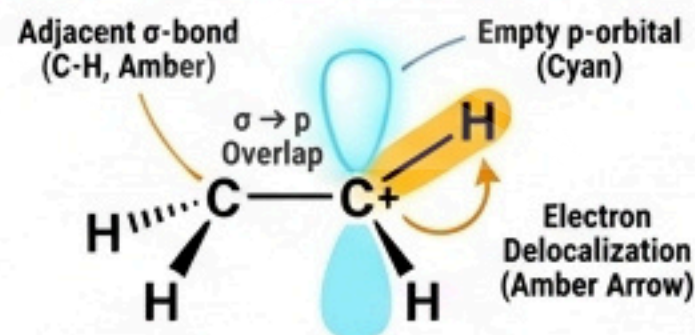
The anatomy, orbital mechanics, and applications of Hyperconjugation.

THE ANATOMY OF HYPERCONJUGATION

Hyperconjugation is the stabilizing interaction of electrons in a σ bond (usually C-H or C-C) with an adjacent empty or partially filled p-orbital or a π -system. It involves the delocalization of σ electrons into the empty orbital, providing overall stability to the molecule.

σ (Sigma) $\rightarrow$ p-orbital / π (Pi) system overlap

ORBITAL MECHANICS: A SPATIAL DIAGRAM



Proper orbital alignment is crucial for overlap.

APPLICATIONS & KEY EFFECTS

↑ Increased Stability

Stabilizes carbocations, radicals, and alkenes.



Enhanced Reactivity

Influences reaction rates and selectivity (e.g., Markovnikov's rule).

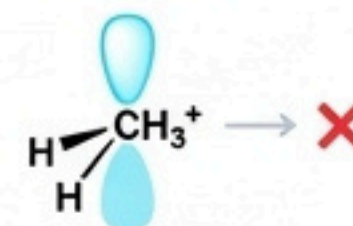


Altered Bond Lengths

Shortens the C-C bond, lengthens the C-H bond involved.

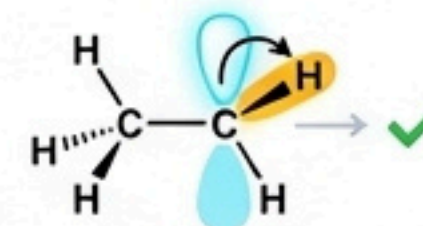
VISUALIZING STABILIZATION: A COMPARISON

✗ Methyl Cation (Unstabilized)



No adjacent σ -bonds for delocalization. Highly unstable.

✓ Ethyl Cation (Stabilized by Hyperconjugation)

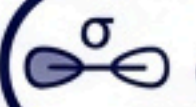


Adjacent C-H σ -bonds overlap with the empty p-orbital. Significantly stabilized.

The electron density from the C-H σ -bond 'spills' into the empty p-orbital, lowering the overall energy of the system.

Defining the Hyperconjugation Interaction

A general stabilizing interaction involving the delocalisation of σ -electrons from an alkyl group's C-H bond.



σ -electrons



Electron p-orbital

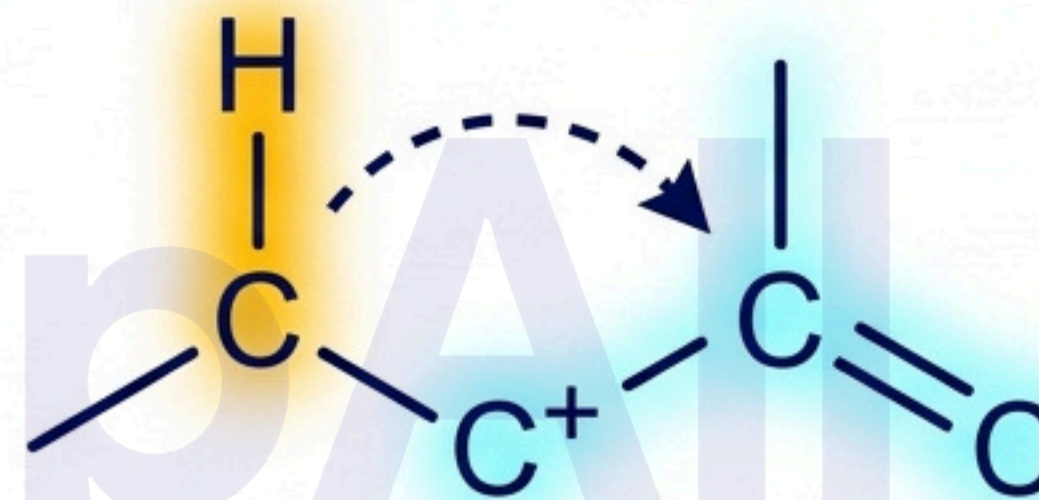


Unshared
p-orbital

OR

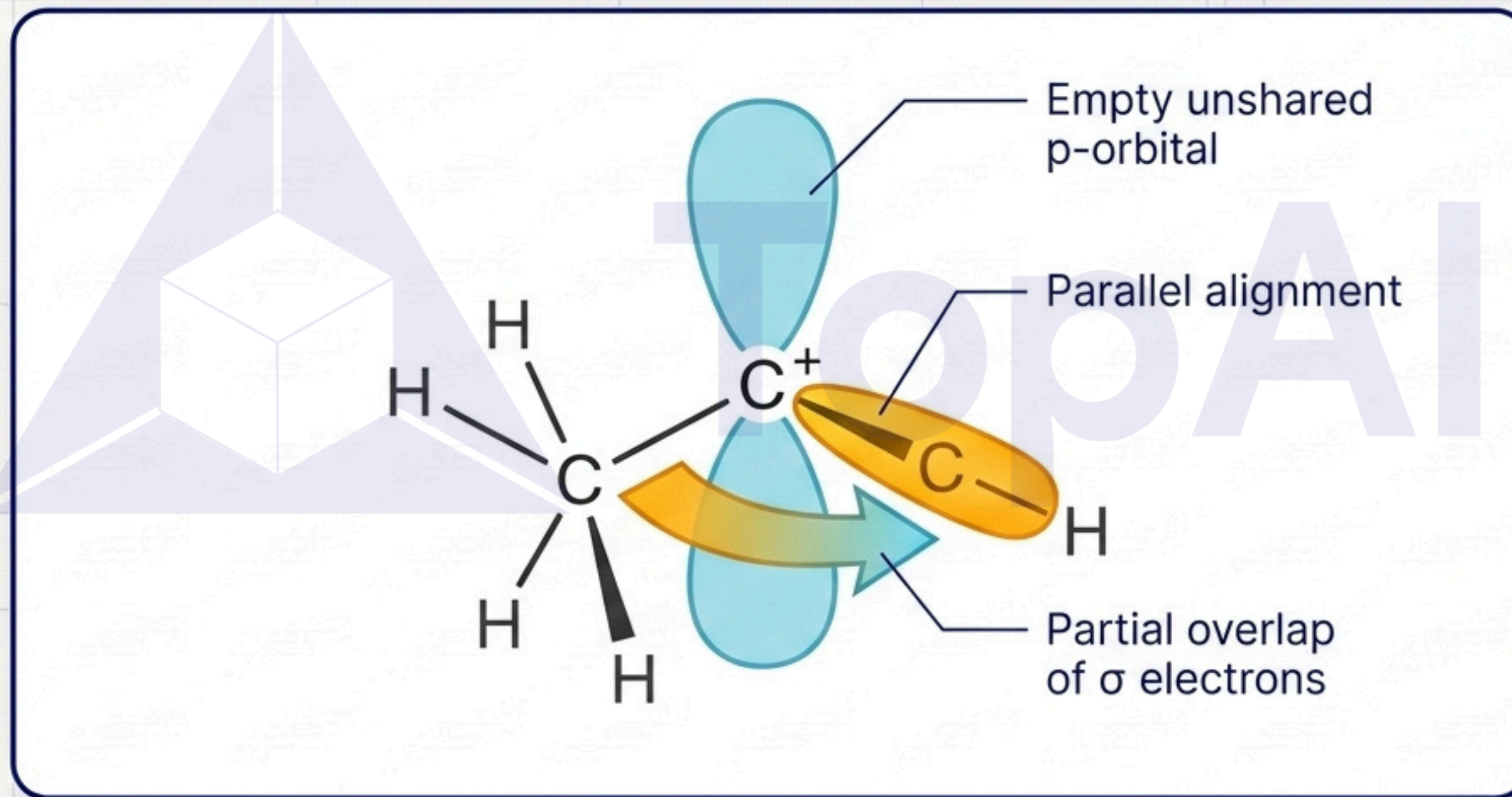


Adjacent
 π -system



The electron density acts as a stabilizer for the adjacent electron-deficient or unsaturated atom.

The Orbital Mechanism: Anatomy of an Overlap





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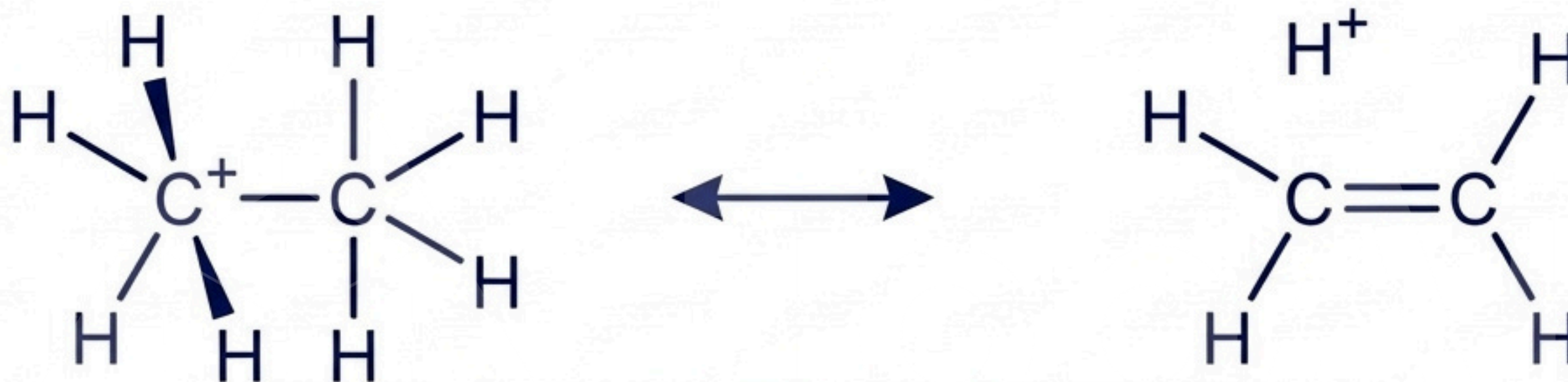
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The 'No-Bond' Paradox

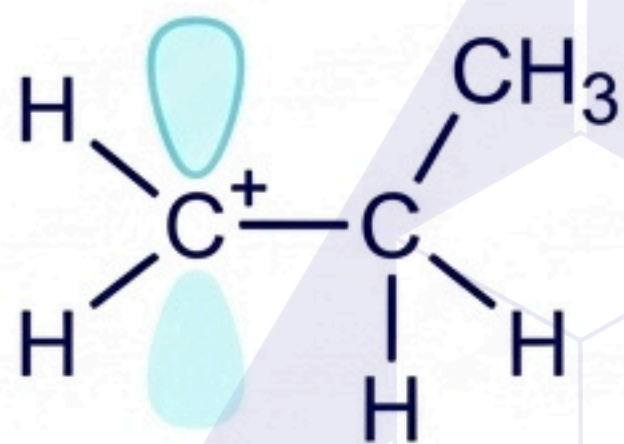


Why 'No-Bond' Resonance?

The bond does not physically break. The 'no-bond' notation is simply a structural drawing convention to represent electron sharing and the dispersal of positive charge. The proton (H^+) remains firmly in place within the spatial field of the molecule.

The Stability Matrix: Carbocations

1° Primary

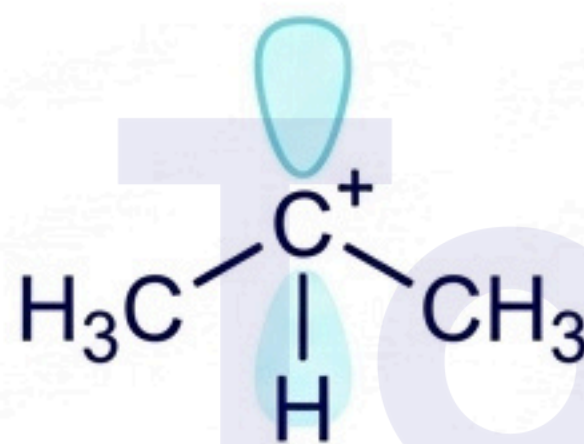


3 α -hydrogens

1/3

Stability

2° Secondary

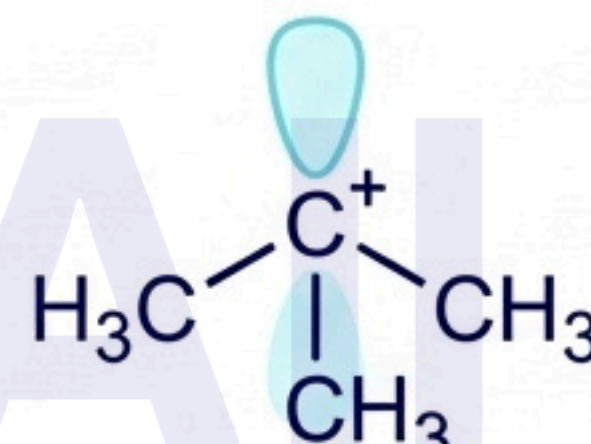


6 α -hydrogens

2/3

Stability

3° Tertiary

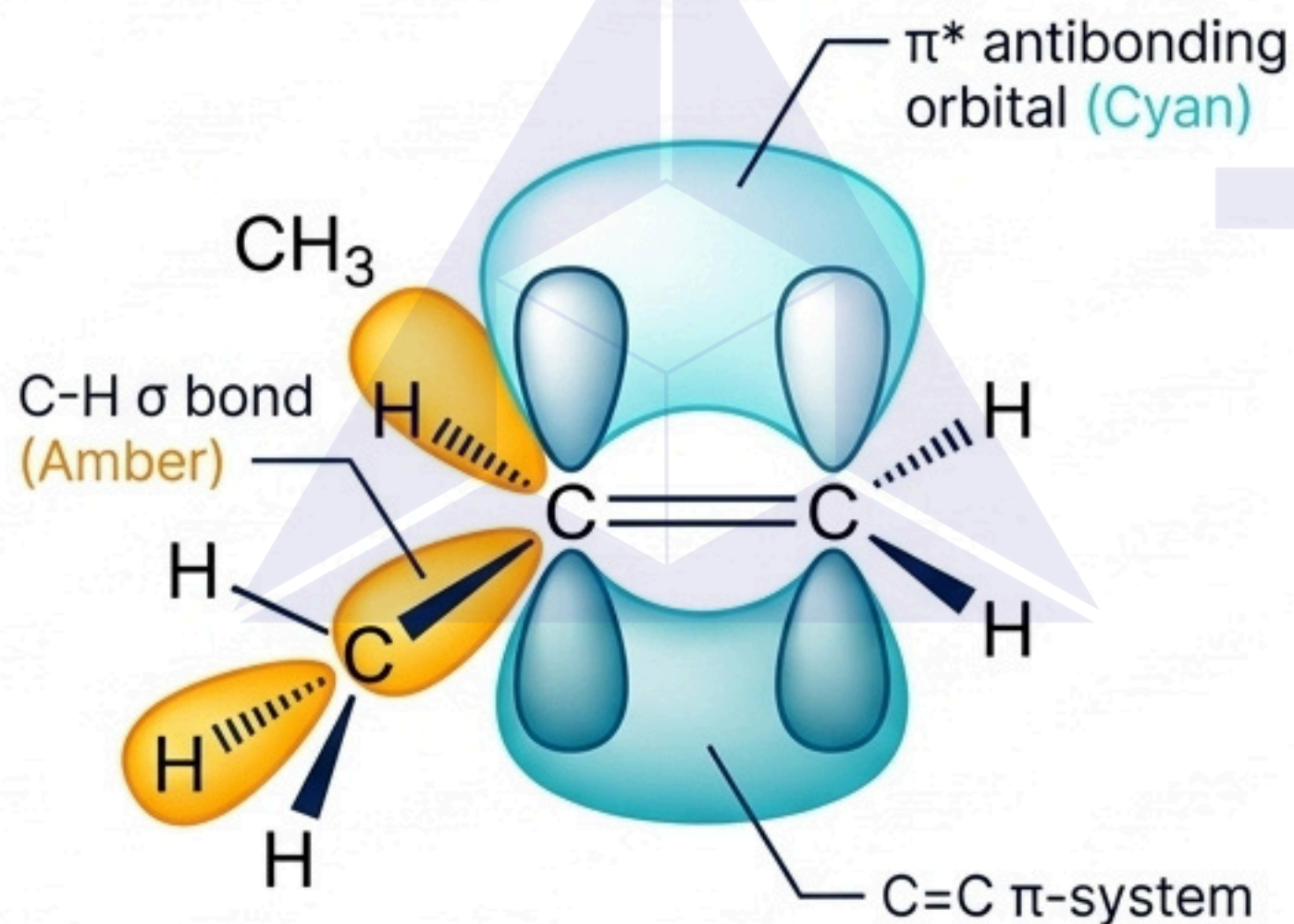


9 α -hydrogens

Stability

More α -hydrogens $\rightarrow$ More hyperconjugation structures $\rightarrow$ Greater dispersal of positive charge $\rightarrow$ Higher Stability

Expanding the Scope: Alkene Stabilization



- Hyperconjugation applies to neutral molecules containing π -systems.
- Delocalisation of C-H σ electrons into the π -system stabilizes the entire alkene structure.

Exam Insight

This mechanism is the fundamental reason behind stability trends in substituted alkenes.

Key Takeaways



The Mechanism

Driven by $\sigma \rightarrow p$ or $\sigma \rightarrow \pi$ orbital overlap. Adjacent C-H bonds must align parallel to the empty or unsaturated orbital.



The Outcome

Results in “no-bond resonance”—a spatial delocalisation of electrons that effectively disperses charge and stabilizes the molecule without breaking bonds.



The Golden Rule

Count the α -hydrogens. A greater number of alkyl groups attached to the unsaturated system yields exponentially greater stability. ($3^\circ > 2^\circ > 1^\circ$).



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