Stereochemistry

Arrangements of Atoms in 3-d Space

Stereochemistry

- The study of the three-dimensional structures of molecules, particularly stereoisomers.

- Structural isomers:
  - Have the same molecular formula, same types of bonds, but different bonding sequences, “connectivity.”

- Stereoisomers:
  - Have the same molecular formula, same bonding sequences, but different spatial arrangements & relative orientations.

Stereochemical *cis-trans* Isomers

- To maintain orbital overlap in the pi bond, C=C double bonds cannot freely rotate.

- Although the two molecules below have the same connectivity, they are NOT identical.

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**Triglycerides & Unsaturated Fatty Acids**

Saturated & Unsaturated: *cis*- vs. *trans-*

**Naming Alkene Stereoisomers:**

the E-Z Notational System vs. “*cis-trans*”
Stereochemical Notation

cis and trans are useful when substituents are identical or analogous

Oleic acid, an unsaturated fatty acid, has a cis double bond. (Hs are identical.)
cis and trans references are ambiguous when analogies are not obvious

Example

A systematic body of rules for ranking substituents must be used, which is related to, but different from the cis and trans references.

The E-Z Notational System

E: higher ranked substituents on opposite sides
Z: higher ranked substituents on same side

Consider each sp² carbon of the double bond separately.
Rank the pair of substituents relative to each other.

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The E-Z Notational System

Compare the pairs

E: higher ranked substituents on opposite sides
Z: higher ranked substituents on same side

(E) Entgegen (Z) Zusammen

The E-Z Notational System

Ranking

The substituents are ranked in order of decreasing atomic number on each carbon.

(E) Entgegen (Z) Zusammen
The Cahn-Ingold-Prelog (CIP) System

The system used was devised by
R. S. Cahn
Sir Christopher Ingold
Vladimir Prelog
Their rules for ranking groups were
devised for another kind of
stereochemistry, chirality, but have been
adapted to alkene stereochemistry.

Example

Higher atomic number outranks lower
atomic number

Br > F      Cl > H

higher Br  Cl higher

lower F    H lower

(Z)-1-Bromo-2-chloro-1-fluoroethene

CIP Rules

When two atoms are identical, compare the
atoms attached to them on the basis of their
atomic numbers. Precedence is established
at the first point of difference.

-CH₂CH₃ outranks -CH₃

higher  C(C,H,H)  lower  C(H,H,H)

CIP Rules

Work outward from the point of attachment,
comparing all the atoms attached to a
particular atom before proceeding further
along the chain.

-CH(CH₃)₂ outranks -CH₂CH₃CH₃

-\(\text{C(C,H,H)}\)  -\(\text{C(C,H,H)}\)

higher  lower

CIP Rules

-CH(CH₃)₂ outranks -CH₂CH₃CH₃

-\(\text{C(C,H,H)}\)  -\(\text{C(C,H,H)}\)

higher  lower
CIP Rules

Evaluate substituents one by one. The ranking is not cumulative: Do not add atomic numbers within groups.

- \( \text{CH}_2\text{OH} \) outranks \( \text{C} (\text{CH}_3)_2 \)
- \( \text{C} (\text{O},\text{H},\text{H}) \) outranks \( \text{C} (\text{C},\text{C},\text{C}) \)

Question

The molecules above are (E) configurations.

True (A)  False (B)

CIP Rules

An atom that has double or triple bonds to another atom is considered to be replicated as a substituent on that atom. See oxygen:

- \( \text{CH}=\text{O} \) outranks \( \text{CH}_2\text{OH} \)
- \( \text{C} (\text{O},\text{O},\text{H}) \) outranks \( \text{C} (\text{O},\text{H},\text{H}) \)

Question

The molecules above are (Z) configurations.

True (A)  False (B)