Relative and Absolute Configuration

Relative configuration compares the arrangement of atoms in space of one compound with those of another. Until the 1950s, all configurations were relative. Absolute configuration is the precise arrangement of atoms in space. We can now determine the absolute configuration of almost any compound.

Relative configuration

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{CH}_2 &\xrightarrow{\text{Pd}} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\
\text{[+]} + 33.2^\circ &\xrightarrow{} \text{[+]} + 13.5^\circ
\end{align*}
\]

No bonds are made or broken at the chiral carbon in this experiment. Therefore, when \((+\) 2-butene-2-ol and \((+\) 2-butanol have the same sign of rotation, the arrangement of atoms in space at the chiral carbon atom is analogous. The two have the same relative configuration.

Two possibilities

```
-CH(OH)-CH(OH)
H    H

But in the absence of additional information, we can't tell which structure corresponds to \((+\) 3-butene-2-ol, and which one to \((-\) 3-butene-2-ol.
```

Two possibilities

```
-CH(OH)-CH(OH)
H    H

Nor can we tell which structure corresponds to \((+\) 2-butanol, and which one to \((-\) 2-butanol.
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Absolute configurations

\[ \text{HO} \xrightarrow{\text{H}_2\text{Pd}} \text{HO} \]

\[ [\alpha]^{+} + 13.5^\circ \]

\[ \text{H} \xrightarrow{\text{H}_2\text{Pd}} \text{OH} \]

\[ [\alpha]^{-} - 13.5^\circ \]

Relative configuration

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{HBr}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \]

\[ [\alpha]^{+} + 33.2^\circ \]

\[ [\alpha]^{-} - 5.8^\circ \]

Not all compounds that have the same relative configuration have the same sign of rotation. No bonds are made or broken at the chiral carbon in the reaction shown, so the relative positions of the atoms are the same. Yet the sign of rotation can change.

Determined Absolute Configuration

Glyceraldehyde
Tartaric Acid


Pasteur - Wine and Absolute Configuration

d- and l- tartaric acid

Absolute Configuration

The \( R,S \) system of nomenclature

Rank the groups (atoms) bonded to the chirality center

1. Rank the substituents at the stereogenic center according to their atomic number.
2. Orient the molecule so that lowest-ranked substituent points away from you. (The back in a 3d drawing.)
3. If the order of decreasing precedence traces a clockwise path, the absolute configuration is \( R \). If the path is anticlockwise, the configuration is \( S \).
Orient the lowest priority (4) away from you

Switch any 2 and it is the opposite configuration.

Clockwise = R configuration
Counterclockwise = S configuration

1. Rank the groups bonded to the asymmetric carbon

2. If the group (or atom) with the lowest priority is bonded by hatched wedge,

3. If necessary, rotate the molecule so that the lowest priority group (or atom) is bonded by a hatched wedge

4. chiral carbon in a ring

-CH₂C=CH₂CH₃ > -CH₃ > -H

A Sleeping Pill or a Potent Teratogen?

The S-isomer is an effective sedative.
The R-is the teratogen in humans.
Which is the one above?

Rules for Fischer projections

Arrange the molecule so that horizontal bonds at chiral carbon point toward you and vertical bonds point away from you.
Projection of molecule on page is a cross. When represented this way it is understood that horizontal bonds project outward, vertical bonds are back.