

Circular Dichroism

Based on Chapter 10 from van Holde Physical Biochemistry

In organic chem learned about isomers, chemical with same formula, but different 3-D structures

Constitutional Isomers: Same formula but different arrangement - will have different physical properties

Stereoisomers: Same arrangement overall, but different placement around tetrahedral centers (sp^3 hybridized atoms) - same physical properties

Interactions with polarized light is only difference.

CD and ORD

Can also have conformational isomers.

Exactly the same Chemical structure, down to placement around all 3D centers

overall 3D arrangement still give different properties

Sometimes physical properties different

Usually CD or ORD properties different

10.1 Polarization of Radiation

fig 10.1

EM wave characterized by amplitude and orientation of Electric and Magnetic vectors

Magnetic and electric vectors always at right angles

Magnetic and electric vectors always perpendicular to direction of propagation

Plane polarized light (figure 10.1)

Note Dan and I get the sense of an error in the figure EX H should go in -X!

Magnetic and electric vectors are in 1 dimension only

(In this case E is Z, H is y)

Direction fixed - amplitude varies

You know def of wavelength and frequency

Easy to make because many crystals or other substances exist the will not let light through unless is polarized along a single axis

(Polaroid sunglasses)

Circularly polarized light (10.2)

Look at E vector only (but H does the same thing)

Here direction varies, amplitude fixed

Can be right or left handed Figure 10.3

Right clockwise as come at you

Left counterclockwise as comes at you

(This doesn't follow modern right and left hand convention - put thumb on direction of propagation and have your fingers

follow the E vector- but may be following older convention -
look at the light if goes to the right is right handed convention
used in plane polarized light)

Notice what happens if you combine a right circularly polarized light with a left?

You get plane polarized

So can think of plane polarized as containing a right and left circularly polarized

What happens if the right and left aren't absorbed equally?

Get elliptically polarized

10.2 CD and ORD

Most stereo isomers are optically active, that is , one isomers will interact differently with polarized light than the mirror image of the compound. We see these interaction in two major phenomena circular dichroism and optical rotatory dispersion. Let's look at both in detail

CD

You already know what absorption of light is. Circular Dichroism occurs because stereoisomers will absorb circularly polarized light slightly differently. Since it is an absorption effect, it is only observed at the wavelengths where a molecule absorbs light. There is a theory behind how this works, and it depends on how the dipole moment of the molecule changes between the ground and the excited state. The theory even works for simple molecules.

Since some molecules absorb right better than left or vice versa, what we plot is $\Delta\epsilon = \epsilon_L - \epsilon_R$ vs. wavelength. So when $\epsilon_L > \epsilon_R$ you get a + number, and when it is reversed a - number. CD interactions are very weak. For something like DNA you will be looking at a total absorbance $\epsilon=3,330$, but a $\Delta\epsilon$ between 1 and 10!. So you are literally observing $\epsilon_L = 3335$ and $\epsilon_R = 3325$. A change of <1%!! See figure 10.6 as example

ORD

Optical rotatory dispersion. Changing the plane of polarization. This effect occurs at ALL wavelengths, not just wavelengths where there are absorption bands. The effect is observed when plane polarized light is passed through a substance. While the light remains plane polarized, the plane of the light is observed to rotate (figure 10.7)

$$\alpha = [\alpha]dC$$

α = observed angle of rotation

$[\alpha]$ = specific rotation

d pathlength (in old convention in decimeters .1m!)

C = concentration (in old convention g/ml)

If look toward the light and rotates clockwise + dextrorotary
Counterclockwise - levorotary

Optical rotation is tied to the refractive index of a material, which is , in turn, tied to light scattering instead of light absorption. That is why it occurs at all wavelengths.

Why?

Plane polarized light composed of right and left circularly polarized light
optical material has slightly different refractive indexes

What happens when add back together = get change in angle of plane! (Figure 10.8)

10.3 Molecular Basis

Skip detailed explanation

Things with in a plane of symmetry will have NO CD or ORD

Things that are mirror images will have OPPOSITE CD and ORD