

# Chiroptical Spectroscopy

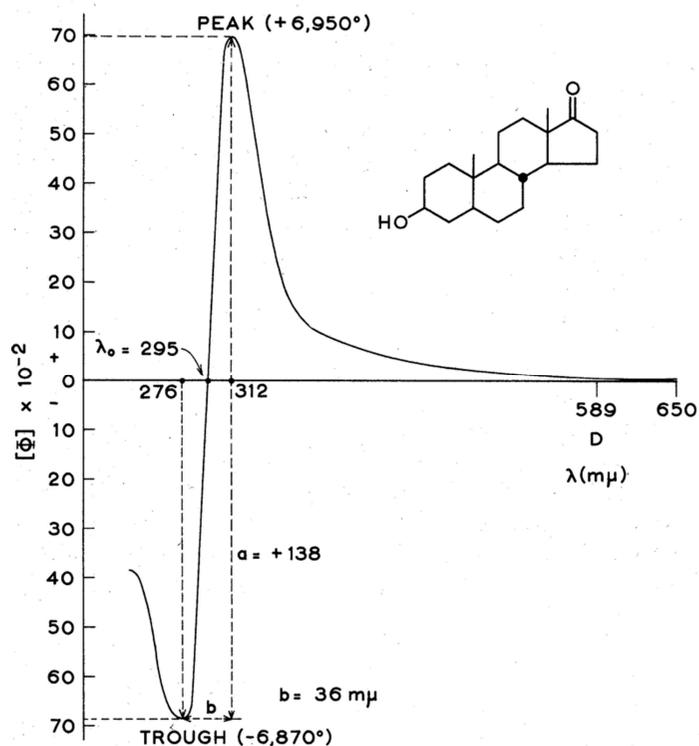
## Theory and Applications in Organic Chemistry

**Lecture 5:** Circular dichroism

**Masters Level Class (181 041)**

Block course, october 2020

# Optical rotation and circular dichroism



## Optical rotation

$$\Delta n = n_L - n_R$$

## Cotton effect:

OR changes sign near absorbance bands

rotational strength of transition  $n \leftarrow 0$

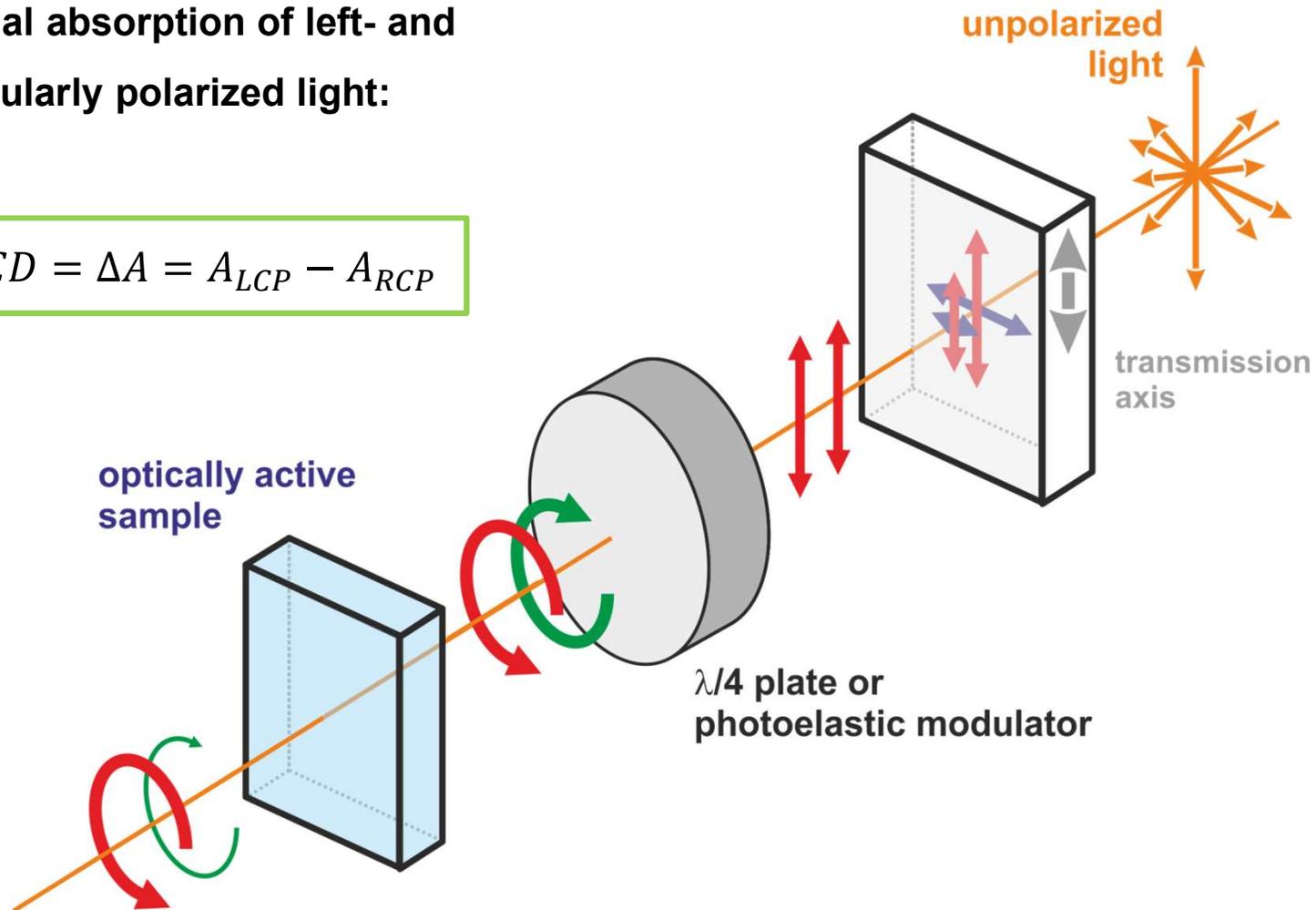
$$R_{n0} = \text{Im}\{\boldsymbol{\mu}_{0n} \cdot \boldsymbol{m}_{n0}\}$$

$\mu$ : electric dipole transition moment (EDTM)  
 $m$ : magnetic dipole transition moment (MDTM)

# Circular dichroism

Differential absorption of left- and right-circularly polarized light:

$$CD = \Delta A = A_{LCP} - A_{RCP}$$



## Units of CD

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**Today:** Difference of absorption coefficients

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R$$

and thus units of  $\text{M}^{-1} \text{cm}^{-1}$

**Historically**, due to association with ORD, one still finds the molar ellipticity  $[\Theta]$ :

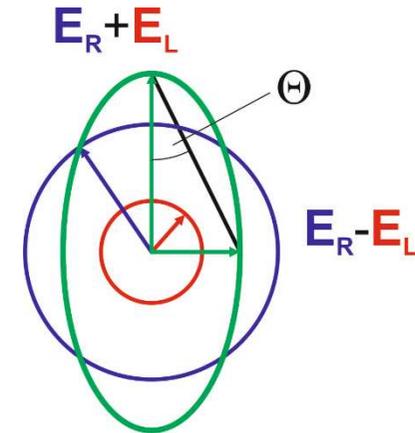
$$[\Theta] = 3298.2 \Delta\varepsilon$$

given in units of degree (respectively  $\text{deg cm}^2 \text{dmol}^{-1}$ )

**Ellipticity:**

$$\tan \Theta = \frac{E_R - E_L}{E_R + E_L}$$

with  $E_R / E_L$  being the field vectors of circular polarized light



As  $\Theta$  is small, it can be approximated that  $\tan \Theta \approx \Theta$

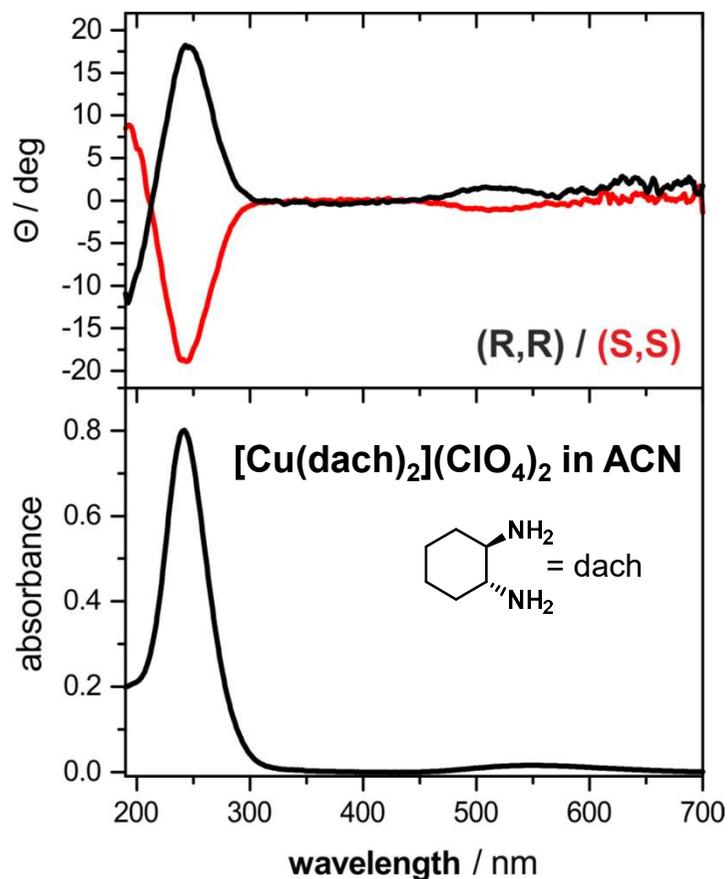
As the light intensity  $I$  is proportional to  $E^2$ :

$$\Theta(\text{radians}) = \frac{I_R^{1/2} - I_L^{1/2}}{I_R^{1/2} + I_L^{1/2}}$$

Since  $\Delta A \ll 1$ , we can use Taylor series to expand the exponentials, and after conversion from radians to degrees, we get:

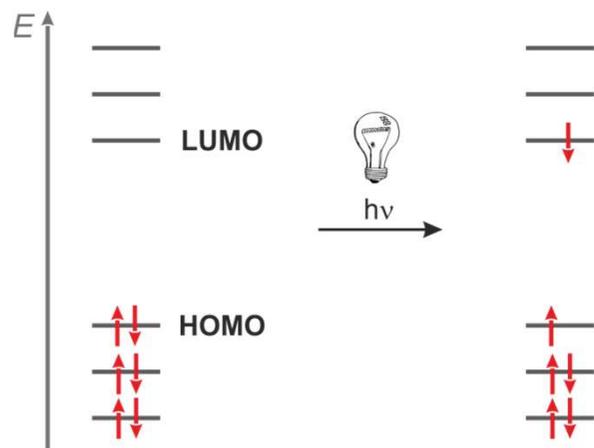
$$\Theta(\text{degrees}) = \Delta A \left( \frac{\ln 10}{4} \right) \left( \frac{180}{\pi} \right) \xrightarrow{[\Theta] = \frac{100\Theta}{cl}} 100 \Delta \varepsilon \left( \frac{\ln 10}{4} \right) \left( \frac{180}{\pi} \right) = 3298.2 \Delta \varepsilon$$

# What do we see in a CD spectrum?

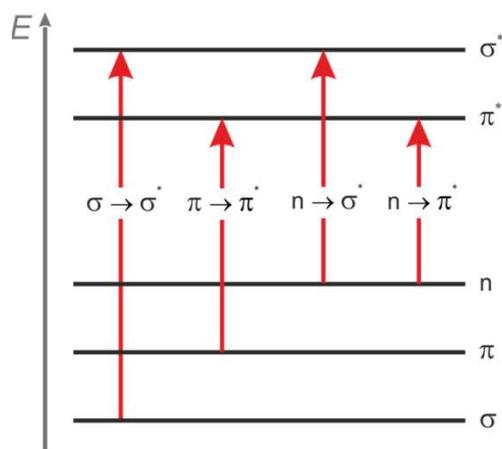


- Every UV/vis band has a CD feature
- Relative intensities do not correlate, i.e. strong UV/vis band does not necessarily feature strong CD band
- Experimental considerations: Comparable to regular UV/Vis, except that OD ideally below 1.0
- Both UV/vis and CD spectrum are collected simultaneously
- Good practice to show both together and not separated
- **Analysis:**
  - a) Empirical rules (knowledge about transitions required!)
  - b) Quantum chemical calculations

## Reminder: Basics of UV/vis excitation processes



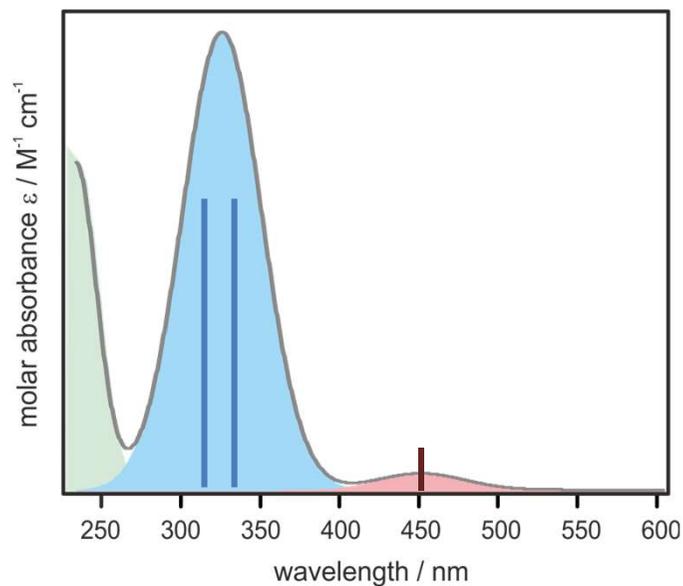
Absorption of a photon excites transition of an electron from an occupied (binding) to an unoccupied orbital.



Not all possible transitions are quantum mechanically allowed (see selection rules), but one frequently observes:

$\sigma \rightarrow \sigma^*$	$\lambda < 180 \text{ nm}$
$\pi \rightarrow \pi^*$	$\lambda > 200 \text{ nm}$
$n \rightarrow \pi^*$	$\lambda > 230\text{-}270 \text{ nm}$
$n \rightarrow \sigma^*$	$\lambda \sim 170\text{-}220 \text{ nm}$

## Reminder: Intensities and absorption coefficients



### Molar absorptivity $\epsilon$

- ... is a measure for the transition probability
- ... proportional to the oscillator strength  
respectively the transition dipole moment

$$\epsilon \leq 10$$

forbidden

$$10 \leq \epsilon \leq 1000$$

weakly allowed

$$1000 \leq \epsilon \leq 100000$$

allowed

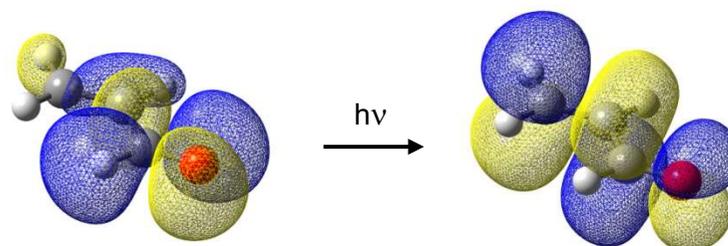
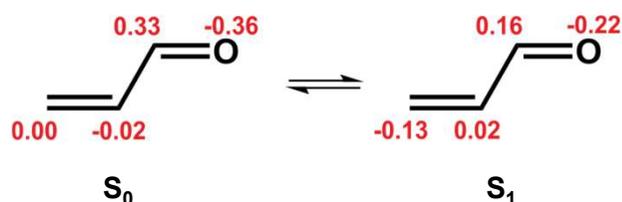
$$100000 \leq \epsilon$$

strongly allowed

# Transition dipole moment

During transition from orbital  $i$  to orbital  $j$ :

Rearrangement of electron density due to „movement of charge“



During relaxation from  $j$  to  $i$ : again rearrangement of charge

... i.e. charge respectively electron density oscillates during electronic transitions

intensity of absorption  $\sim$  degree of charge oscillation

oscillator strength  $f_{ij}$

## Oscillator strength $f$

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Quantification of charge rearrangement:

$$f = \left( \frac{4 \pi m_e \nu_{fi}}{3 e^2 \hbar} \right) |\mu_{fi}|^2$$

If electric dipole moment...

$\mu = 0$ : electric dipole forbidden

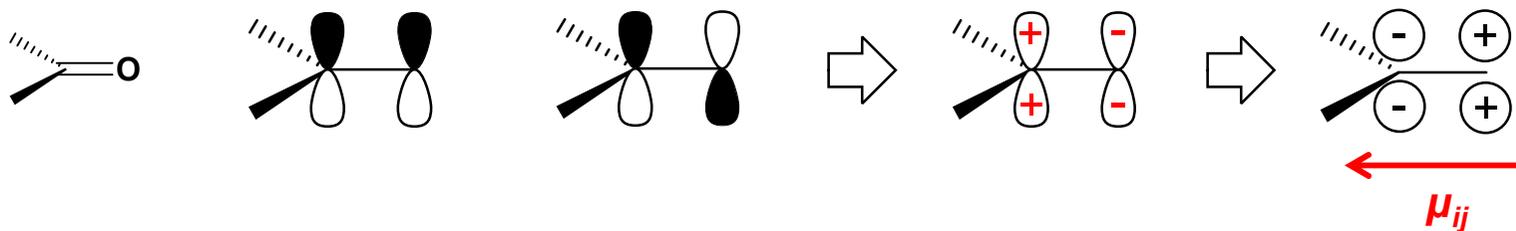
$\mu \neq 0$ : electric dipole allowed

# Qualitative determination of edtm

## Procedure to determine $\mu_{ij}$ :

- 1) Identify participating MOs
- 2) Multiply the MOs and determine signs of „product orbitals“
- 3) Invert signs to obtained charges from electron density
- 4) Do the product MOs have dipolar character?

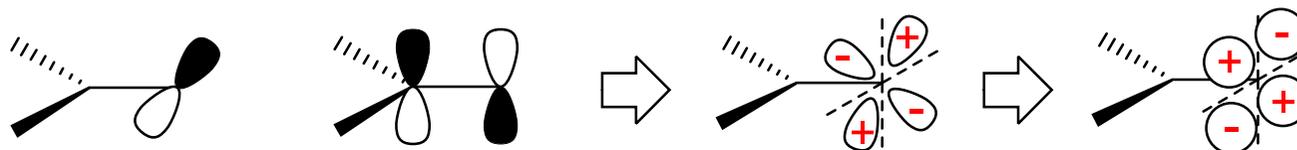
## $\pi \rightarrow \pi^*$ of a C=O group



Large edtm for  $\pi \rightarrow \pi^*$  transition, i.e. strong absorbance band

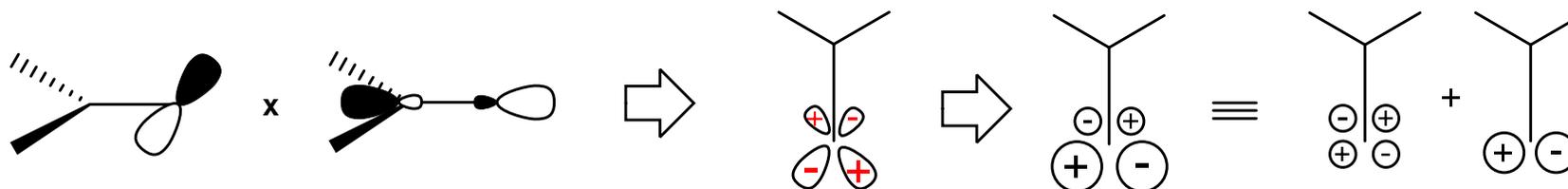
## More examples for edtm determination

### $n \rightarrow \pi^*$ of a C=O group



Quadrupole moment, but not dipole moment, i.e. forbidden transition

### $n \rightarrow \sigma^*$ of a C=O group

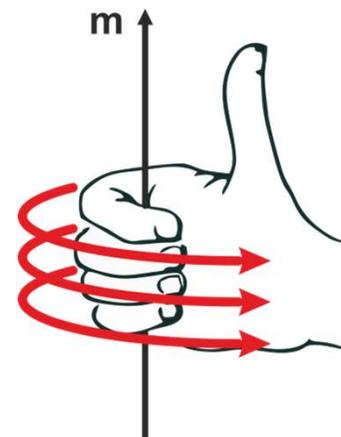


- Product MO not evenly distributed around oxygen and orthogonal to the C-O bond
- Can be split into weak quadrupole and medium dipole moment  $\rightarrow$  allowed transition (medium intense)

# The magnetic dipole transition moment $m_{ij}$

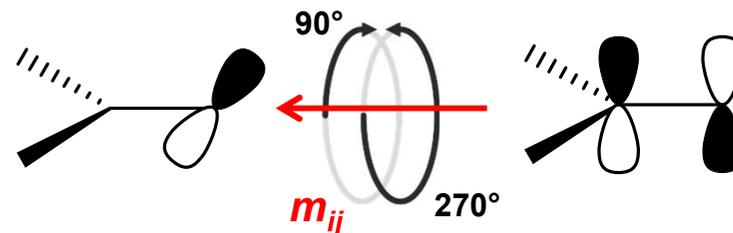
If charge is rotated instead of linearly displaced, according to the right hand rule, we obtain a

*Magnetic dipole transition moment  $m_{ij}$*



## Procedure to determine $m_{ij}$ :

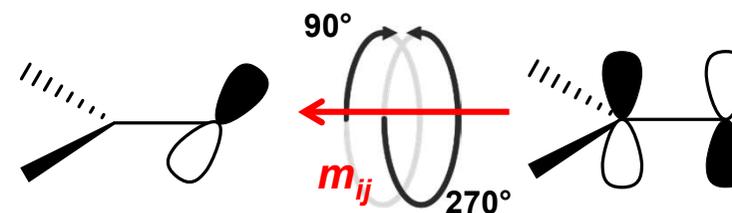
- 1) Identify participating MOs
- 2) Is charge/electron density rotated?  
If yes, is the angle  $\neq 180^\circ$ ?
- 3) Use smaller possible angle for rotation, curl fingers around rotation direction
- 4) Thumb points along magnetic dipole transition moment



# The magnetic dipole transition moment $m_{ij}$

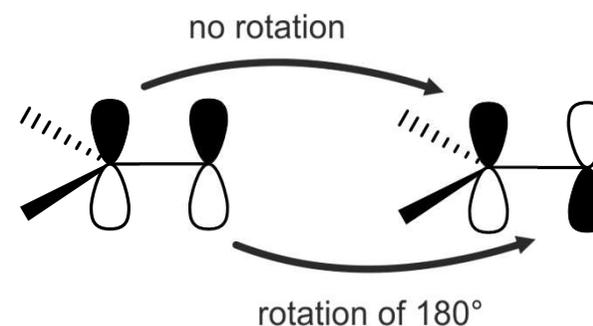
## $n \rightarrow \pi^*$ of a C=O group

Strong magnetic moment  
(transition electronically forbidden,  
but magnetically allowed)



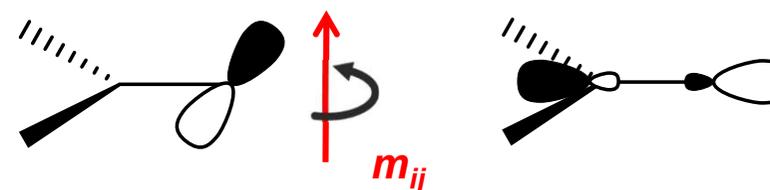
## $\pi \rightarrow \pi^*$ of a C=O group

No magnetic dipole moment



## $n \rightarrow \sigma^*$ of a C=O group

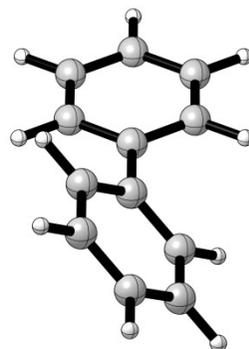
Both electronically and  
magnetically allowed!



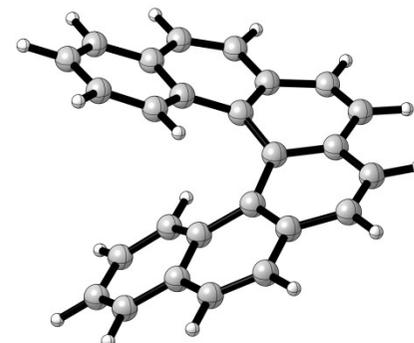
# Classification of chromophores

## Chiral compounds with inherently chiral chromophores

- Chromophoric system is chiral, i.e. due to twist
- Usually very strong CD intensity



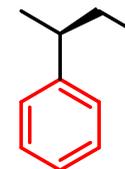
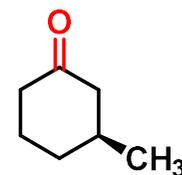
(M)-biphenyl



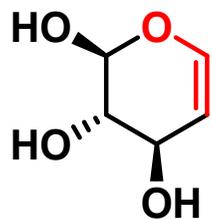
(P)-hexahelicene

## Chiral compounds with achiral chromophores

- More common, i.e. chiral carbonyl compounds
- Achiral chromophore is influenced by chiral environment
- Intensities up to two orders of magnitude smaller

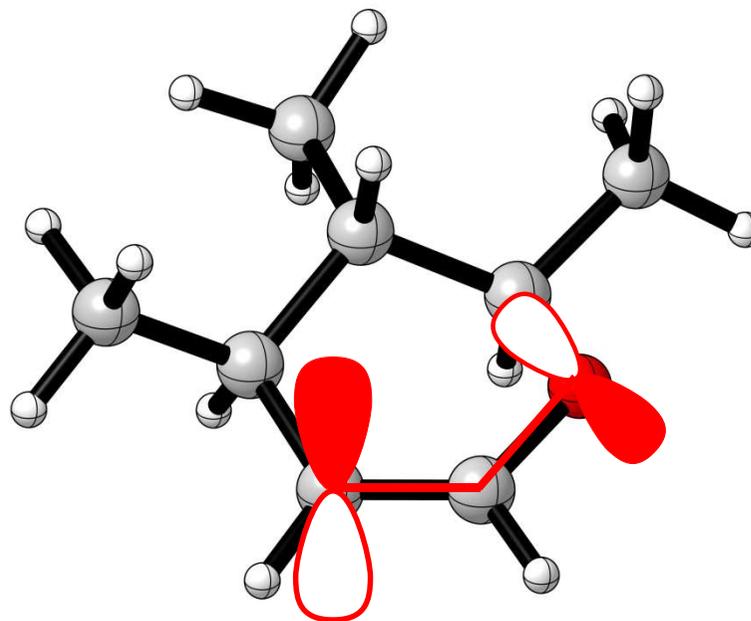
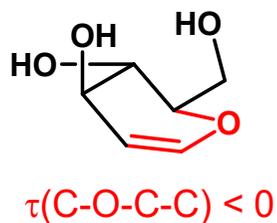
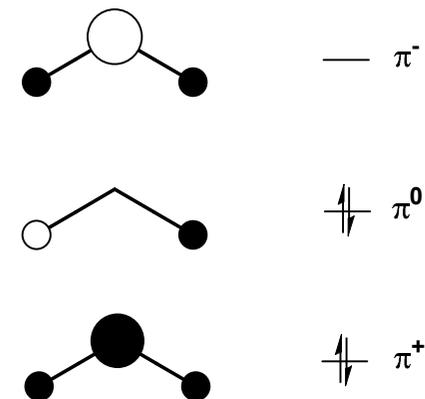


# Determining the sign of CD bands from MO analysis – enol ether

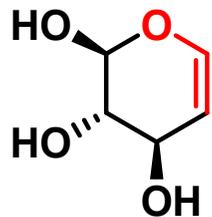


Enol ether is chromophore of  $\pi-\pi^*$  transition

Isoelectronic with allyl anion  $\rightarrow$

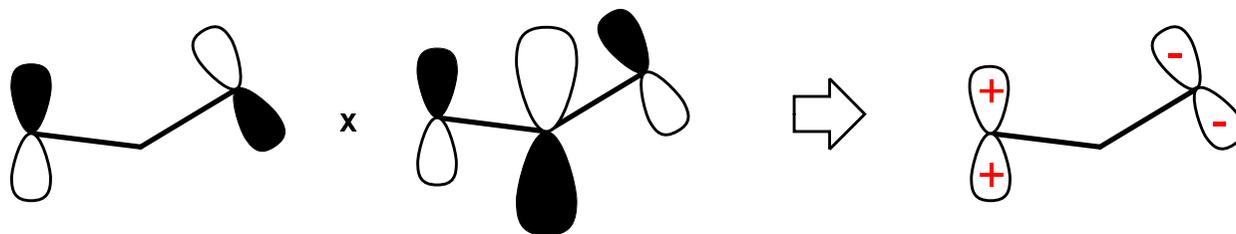
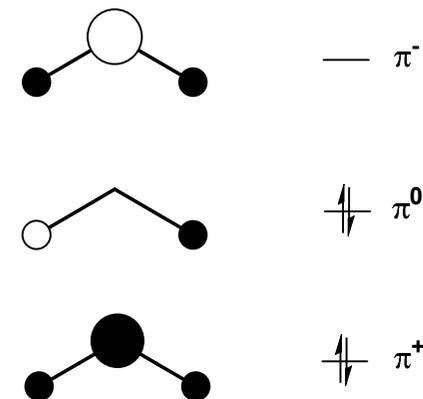


# Determining the sign of CD bands from MO analysis – enol ether

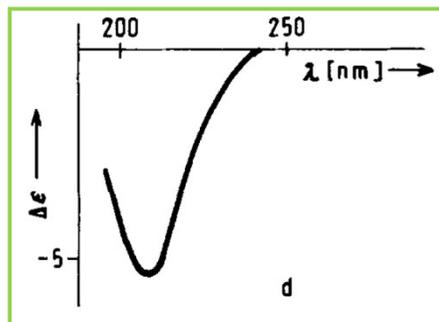


Enol ether is chromophore of  $\pi$ - $\pi^*$  transition

Isoelectronic with allyl anion  $\rightarrow$



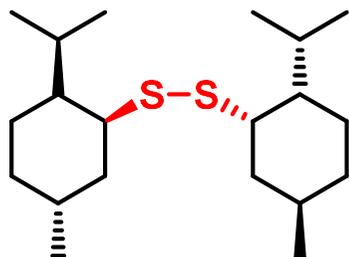
$\mu \downarrow \uparrow m$



**Note:**  
EDTM (+)  $\rightarrow$  (-)  
MDTM Movement of orbital lobes

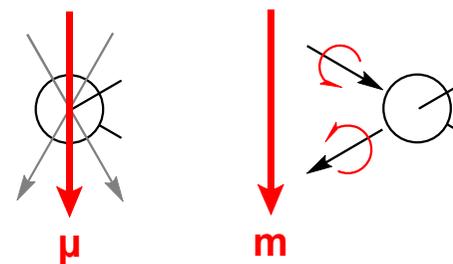
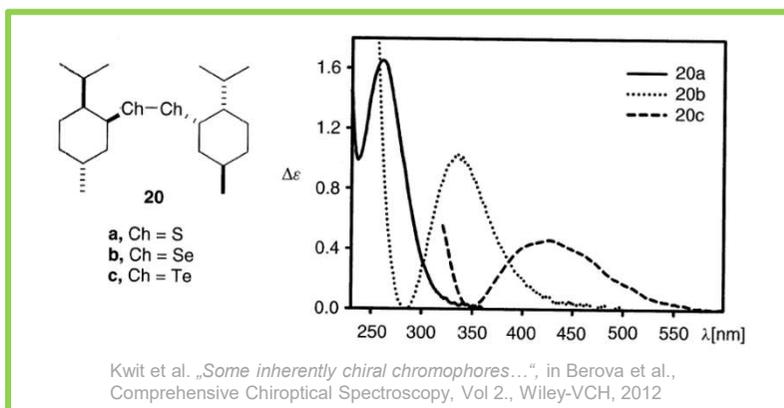
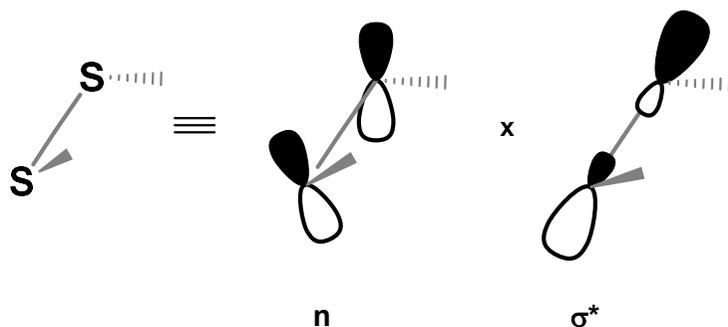
G. Snatzke, *Angew. Chem. Int. Ed. Engl.* **18** (1979) 363-377

# Determining the sign of CD bands from MO analysis - disulphides



Preferred conformation of –S-S- bond features torsional angle of  $\pm 90^\circ$  due to lone pair repulsion.

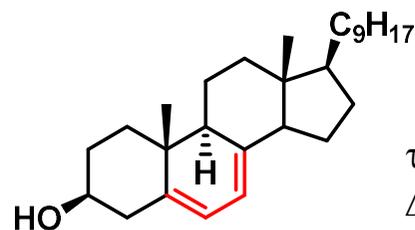
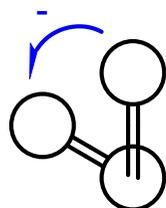
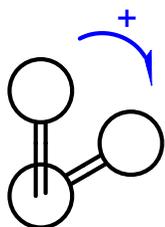
➤ Inherently chiral chromophore with  $n \rightarrow \sigma^*$  transition



# Determining the sign of CD bands – Dienes

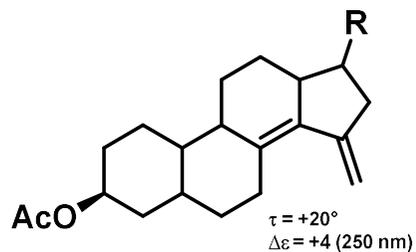
## Diene helicity rule (DHR):

Sign of torsional angle = sign of CD band

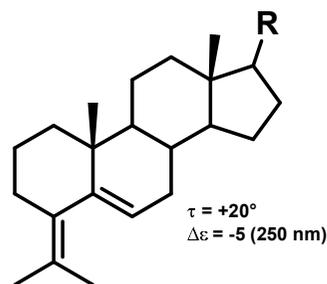


$$\tau = -11^\circ$$
$$\Delta\epsilon = -18.0 \text{ (269 nm)}$$

DHR often valid, but fails for certain types of dienes:



$$\tau = +20^\circ$$
$$\Delta\epsilon = +4 \text{ (250 nm)}$$

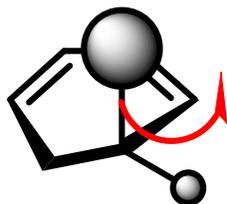


$$\tau = +20^\circ$$
$$\Delta\epsilon = -5 \text{ (250 nm)}$$

# Determining the sign of CD bands – Dienes



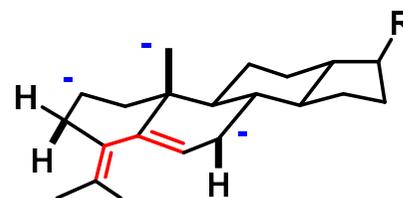
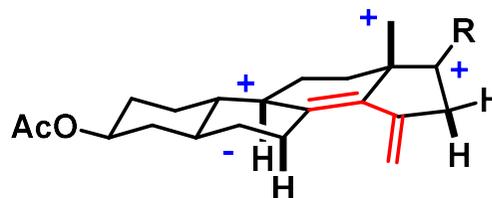
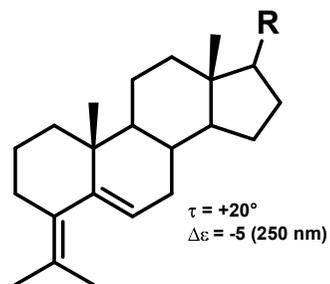
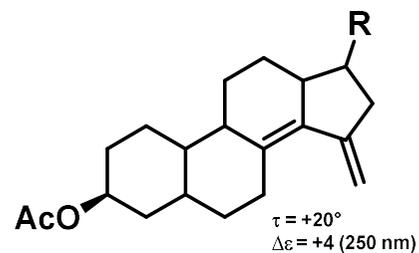
**+CE**  
for right-handed angle  
 $C_{ax}-C_{allyl}-C=C$



**-CE**  
for left-handed angle  
 $C_{ax}-C_{allyl}-C=C$

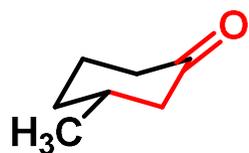
## Allylic Axial Chirality Rule (AACR)

**!** There are many other refined sets of rules for special cases, better check literature before applying them.

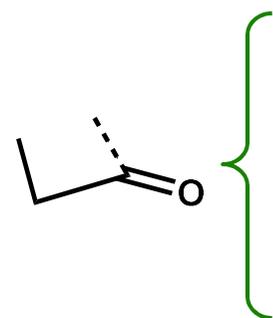


# The $n\text{-}\pi^*$ transition in cyclic carbonyl compounds

G. Snatzke, *Angew. Chem. Int. Ed. Engl.* 18 (1979) 363-377

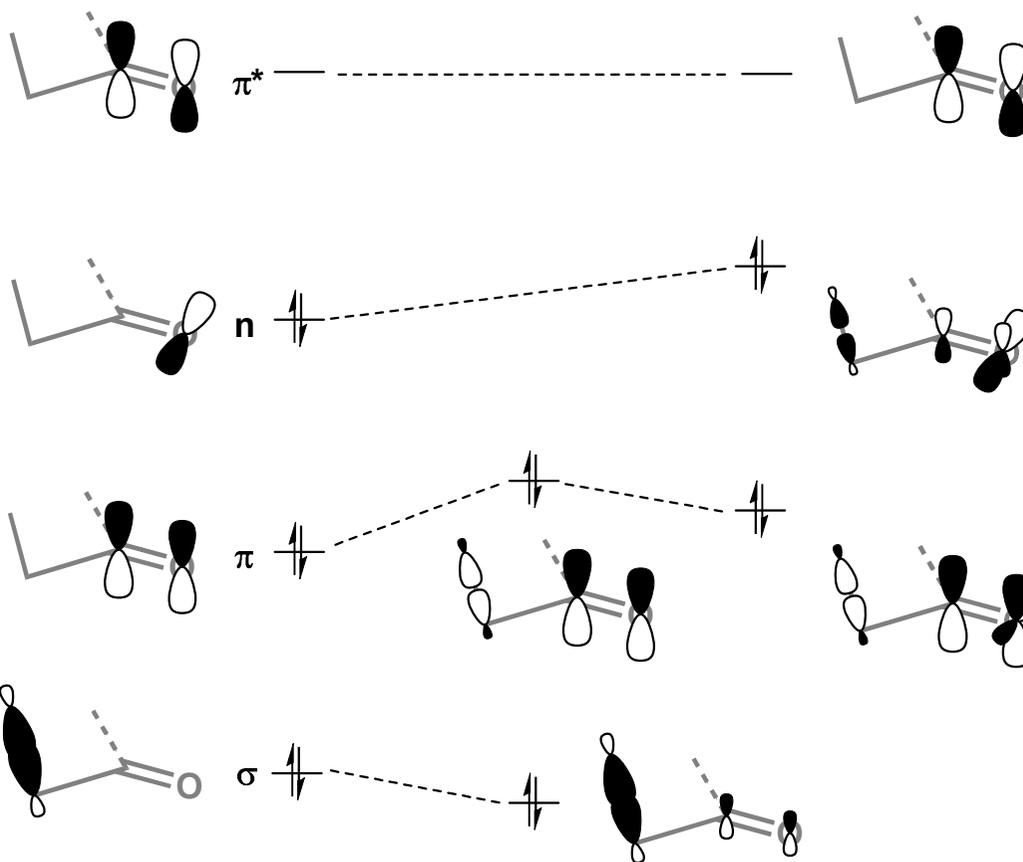


➤ Ideal model for chromophore in chiral environment

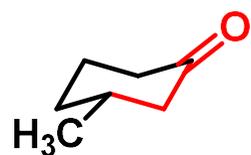


isolated  
chromophore

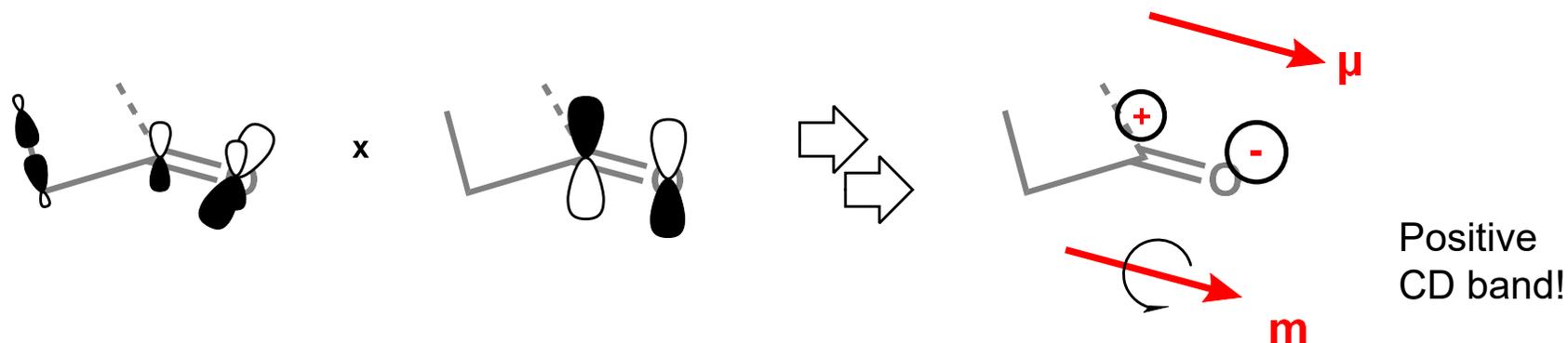
chiral perturbed  
chromophore



## The $n-\pi^*$ transition in cyclic carbonyl compounds



➤ Ideal model for chromophore in chiral environment

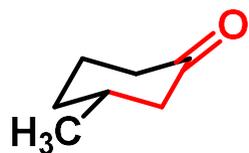


Note:

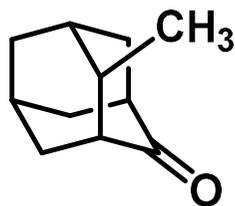
The farther away the perturbing chiral bond, the smaller its influence!

G. Snatzke, *Angew. Chem. Int. Ed. Engl.* **18** (1979) 363-377

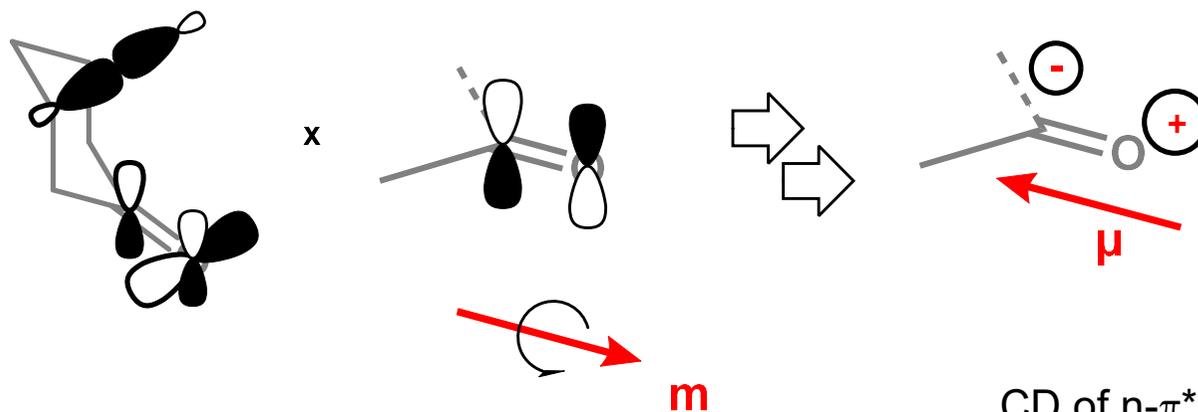
# The $n-\pi^*$ transition in cyclic carbonyl compounds



- Ideal model for chromophore in chiral environment



- Different orbital mixing situation: methyl group situated above C=O bond



CD of  $n-\pi^*$  negative,  
experiment: -0.06

# Octant rule

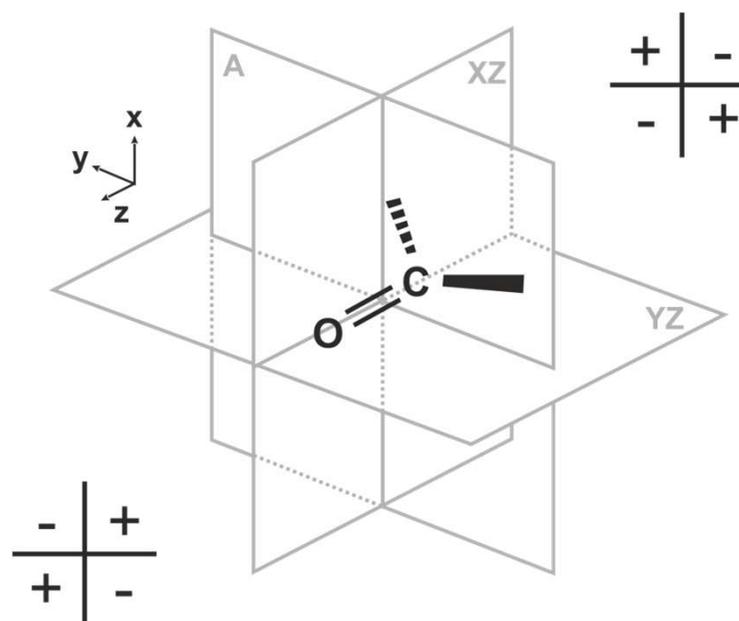
Moffitt, Woodward, Moscovitz, Klyne, Djerassi, *J. Am. Chem. Soc.* **83** (1961) 4013

Originally developed and tested for ORD of steroids on basis of large amount of data by Djerassi, Klyne, and Ourisson, then generalized and transferred to ECD:

Determination of CD sign of the  $n \rightarrow \pi^*$  transition in chiral ketones and aldehyds (~290-300 nm)

Applicable if preferred conformation is known

Or vice versa: If configuration is known, the most preferred conformation can be determined.



# Octant rule

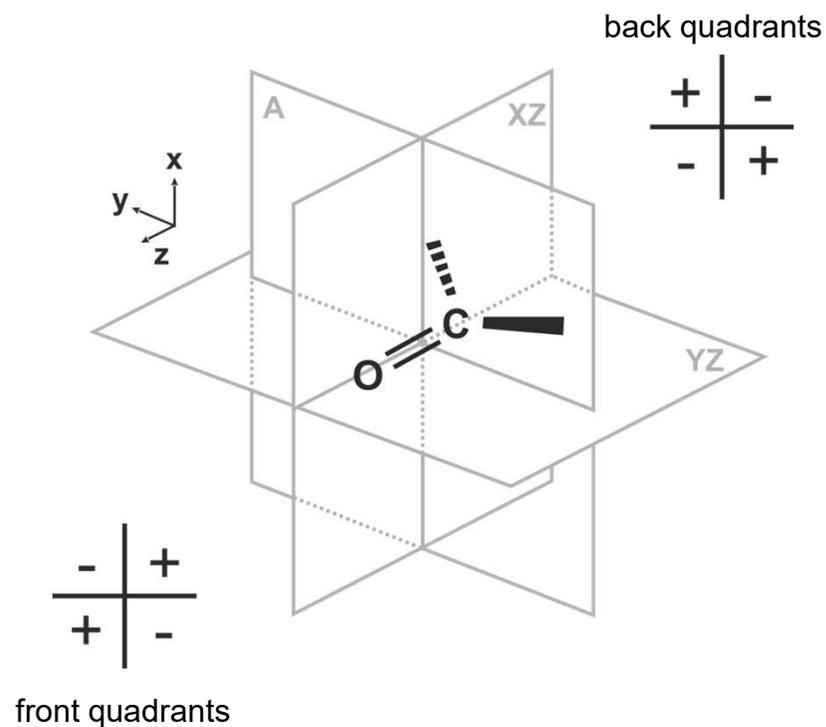
Moffitt, Woodward, Moscovitz, Klyne, Djerassi, *J. Am. Chem. Soc.* **83** (1961) 4013

## Preparation:

- Consider molecule as „substituted formaldehyd“
- Planes of symmetry of formaldehyd are used to define eight octants
- A sign is assigned to each octant

## Analysis:

- Place substituents in rear octants
- Sign of octant = sign of CD band, while substituents closer to the carbonyl have larger contribution
- Number of substituents in (+) and (-) octant = no CD band

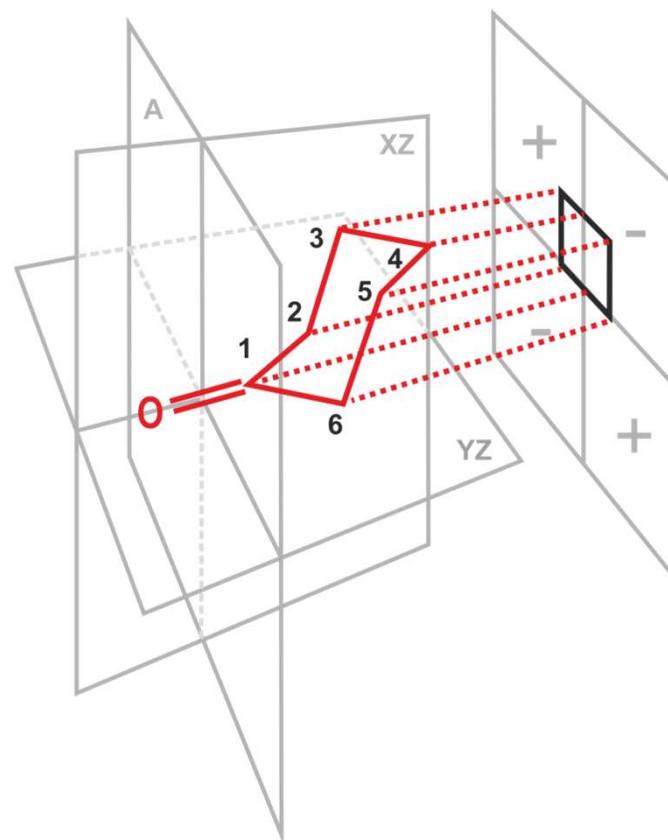


## Octant rule: Example of cyclohexanone

### Cyclohexanone (achiral)

- Assume chair conformation
- Project position of each substituent
- Due to symmetry plane XZ, identical number of atoms in (+) and in (-) octants

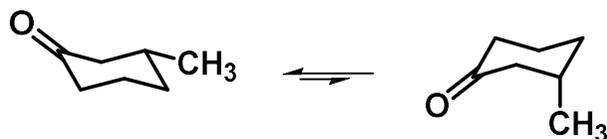
→ No CD band for  $n-\pi^*$  transition



# Octant rule: Methyl cyclohexanone

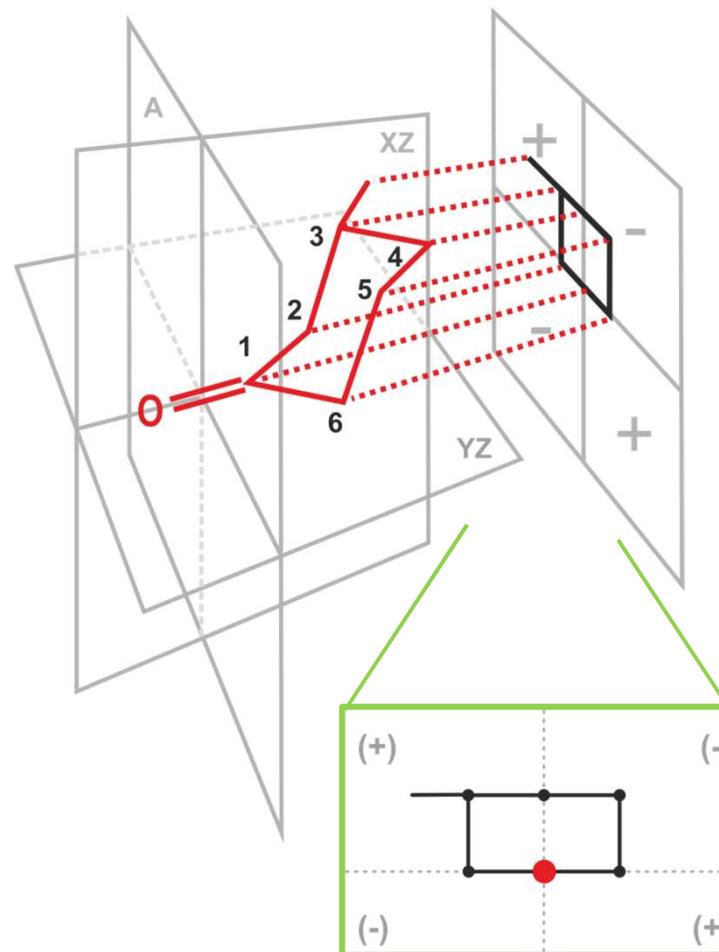
## 3-Methyl cyclohexanone

- Assume chair conformation with methyl group in equatorial position

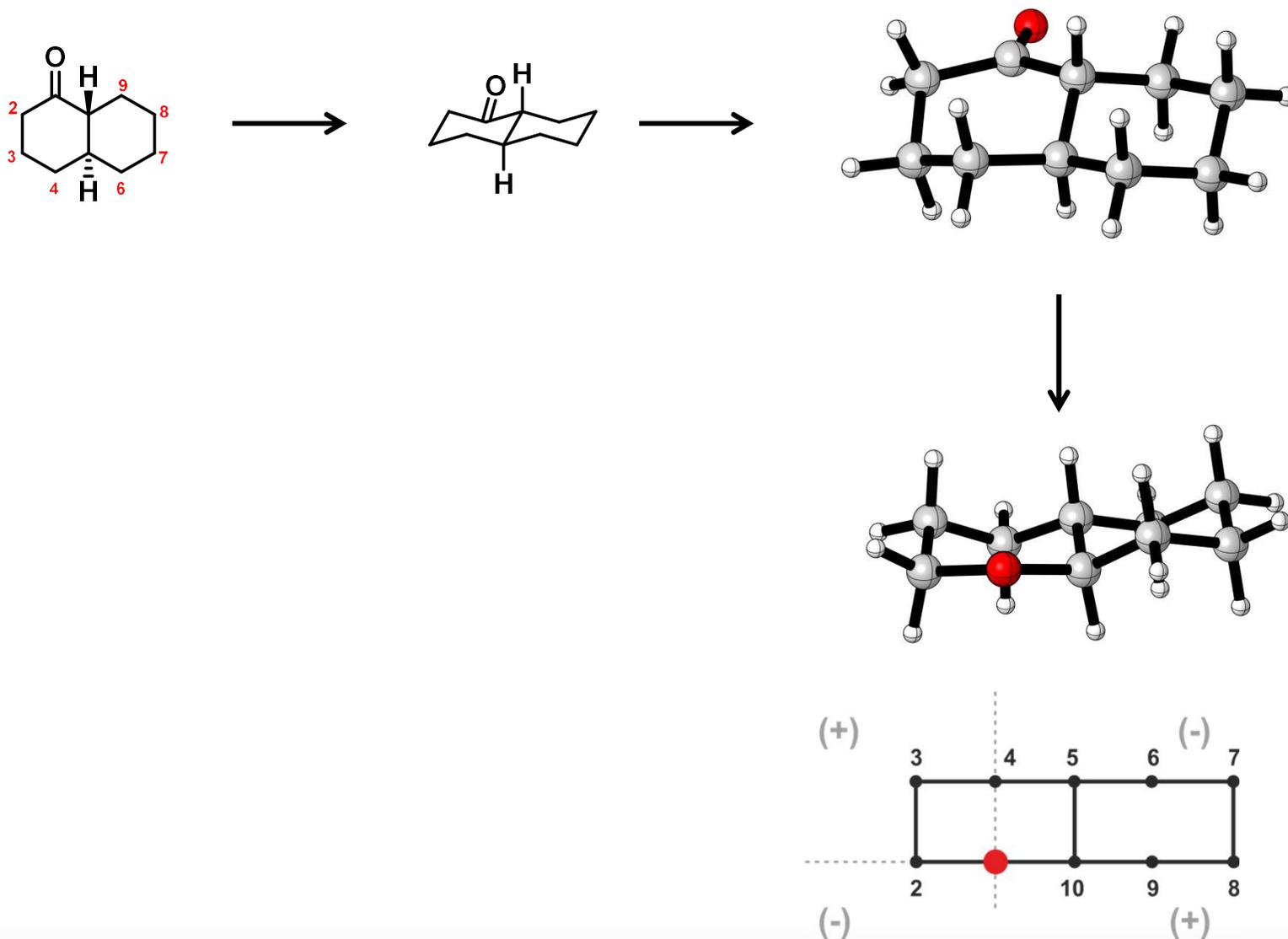


- Methyl substituent in (+)-octant

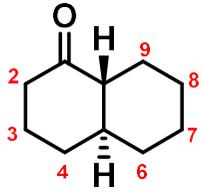
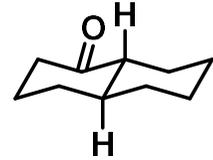
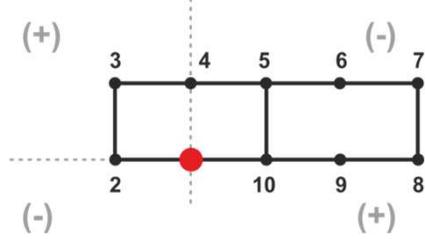
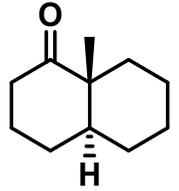
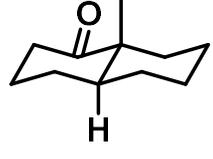
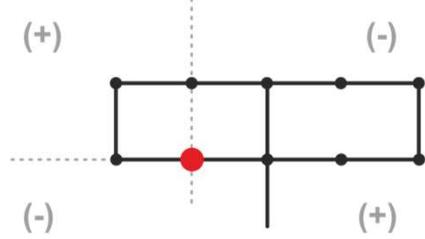
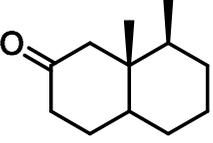
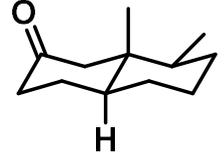
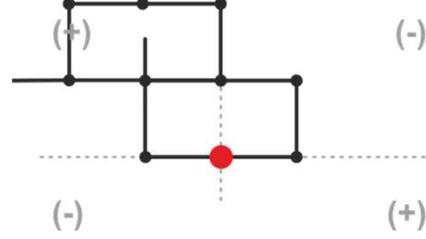
→ Positive CD band for  $n-\pi^*$  transition



# Examples for the octant rule: The orientation confusion



# Examples for the octant rule

Structure	Conformation	Octant Projection	Cotton effect Pred. / Exp.
			- / -
			+ / + methyl group closer to C=O
			+ / +

# Examples for the octant rule

Structure	Octant Projection	Cotton effect Pred. / Exp. $\Delta\epsilon$
		(+) / + 2.1
		(+) / + 5.4
		(+) / + 0.6
		(+) / + 1.2

Geometry of 5-rings  
contributes to CD signal!

# Outline of the lecture

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<b>Dates</b>	<b>topics</b>	
✓ Monday	Introduction	
✓	Polarization of light	
✓ Tuesday	Theoretical basis of optical activity	
✓	Optical rotation	
✓ Wednesday	Circular dichroism	
	Circular dichroism	
Thursday	Vibrational optical activity	
	Vibrational optical activity	
Oct 22?	applications	} your part
Oct 29?	applications	

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