

March CUME

Organic Chemistry

Department of Chemistry, University of Missouri—Columbia
Saturday, March 21, 1998, @Nine O'Clock, 221 Chemistry

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Announced Reading

“Circular Dichroism and Exciton-Coupled Circular Dichroism”

bi.refr. gence *n* [ISV] (1898): the refraction of light in an anisotropic material (as calcite) in two slightly different directions to form two rays -- **bi.refr. gent** *adj*

di.chro.ism *n* (1819): the property of some crystals and solutions of absorbing one of two plane-polarized components of transmitted light more strongly than the other; also: the property of exhibiting different colors by reflected or transmitted light--compare circular dichroism.

circular dichroism *n* (ca. 1961) 1: the property (as of an optically active medium) of unequal absorption of right and left plane-polarized light so that the emergent light is elliptically polarized 2: a spectroscopic technique that makes use of circular dichroism.

Definitions from Britannica Online. Search "circular dichroism" Britannica Online.

<http://www.eb.com:180/cgi-bin/g?DocF=dict/ci/circular_dichroism.html> [Accessed 07 March 1998].

Question 1. Polarized Light, Circular Birefringence and Circular Dichroism. (60 points)

(a) In area 1, draw a schematic diagram of **unpolarized** light. In area 2, draw a schematic diagram of **plane or linearly polarized** light. In both of these cases, draw the **E**-field vector direction(s) and assume that you are looking along the direction the light is traveling (z-direction). In area 3, draw a linearly polarized light wave as a function of time assuming that the light travels in the z-direction (left to right) and is linearly polarized in the xz-plane. In area 4, draw a linearly polarized light wave as a function of time assuming that the light travels in the z-direction (left to right on paper) and is linearly polarized in the yz-plane. (8 points)

Area 1 (2 points)	Area 2 (2 points)
Area 3 (2 points)	
Area 4 (2 points)	

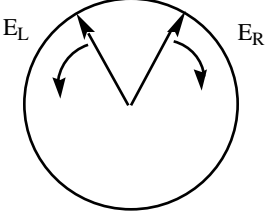
(b) Now let's turn to **circularly polarized light**. Some text follows from the text "Organic Structural Spectroscopy" by Lambert *et al.* (Prentice Hall, 1997). Fill in the blanks. Then read the legend to the Figure (adapted from **Figure 10-10** of the text by Lambert *et al.*) and create the four sketches that the figure legend describes. (12 points)

(Lambert *et al.*, p. 260): _____ (linearly polarized, unpolarized) light might be decomposed into a pair of orthogonal polarization states that are important in understanding chiroptical phenomena: left and right circularly polarized light. In the case of circularly polarized light, the transverse vibrations [of the **E**-field vector] trace out a helix as a function of time. The helix may be either left-handed (top in Figure) or right-handed (bottom in Figure). Viewed in cross-section, that is, if an observer were situated on the z-axis looking toward the light source, the transverse vibrations would trace out a _____. Light whose electric field vector traces out a right-handed helical pattern is termed _____ light. The cross-sectional appearance of _____ (clockwise, counter-clockwise) rotation of the electric field is obtained by pushing the helix forward through a perpendicular plane without rotating it. In other words, the helix is moved forward, but it is not turned like a mechanical screw. (1 point for each blank, 4 total)

(2 points)	(2 points)
(2 points)	(2 points)

Figure. Circularly polarized radiation. Left: The light wave as a function of time. Right: Cross section of the light wave. Light polarized (top) left circularly and (bottom) right circularly.

(c) The components \mathbf{E}_L and \mathbf{E}_R of left and right circularly polarized light are shown in area 1 for some linearly polarized light. First, draw the \mathbf{E} -field resulting from vector addition of the components. Pay attention to direction and magnitude. In areas 2-6, draw the situations after \mathbf{E}_L and \mathbf{E}_R have rotated an additional thirty degrees each, that is, both components move at the same speed. (12 points)

area 1 	area 2	area 3
area 4	area 5	area 6

(d) Do as in (c) but assume that \mathbf{E}_L and \mathbf{E}_R move at different speeds. Assume that \mathbf{E}_L moves 45 degrees in the time \mathbf{E}_R requires to move 30 degrees. Again, draw the resulting \mathbf{E} -field obtained by vector addition of the components. Pay attention to direction and magnitude. In areas 2 and 3, draw the situations after the components \mathbf{E}_L and \mathbf{E}_R have rotated two and three times longer. (6 points)

area 1	area 2	area 3
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State the overall effect resulting from this phenomenon of “circular birefringence” (2 points):

(e) Consider situation (c) and assume that \mathbf{E}_L and \mathbf{E}_R are absorbed equally as they travel through a material. State what happens to the direction of the plane of the polarized light and state what happens to the vector sum of the \mathbf{E}_L and \mathbf{E}_R as time progresses. State what type of polarized light comes out of the material. (7 points)

(f) Consider situation (c) and assume that \mathbf{E}_L and \mathbf{E}_R are absorbed to a different degree (circular dichroism) as they travel through a material. State what happens to the direction of the plane of the polarized light and state what happens to the vector sum of the \mathbf{E}_L and \mathbf{E}_R as time progresses. State what type of polarized light comes out of the material. (7 points)

(g) Consider situation (d) (circular birefringence) and assume that \mathbf{E}_L and \mathbf{E}_R are absorbed to a different degree (circular dichroism) as they travel through a material. State what happens to the direction of the plane of the polarized light and state what happens to the vector sum of the \mathbf{E}_L and \mathbf{E}_R as time progresses. State what type of polarized light comes out of the material. (6 points)

Question 2. Circular Birefringence and Circular Dichroism Quantities. (20 points)

(a) Circular birefringence measurements aim at quantifying the difference in the speeds of left and right polarized light. Circular birefringence measures “optical rotation”. Write down the equation that defines the “specific rotation” and give its units. Write down the equation that defines “molar rotation” and gives its units.

Specific rotation: (5 points)

Molar rotation: (5 points)

(b) Circular dichroism measurements aim at quantifying the difference in the absorbances of left and right polarized light. Most CD instruments measure “angle of ellipticity” vs. θ , which can be adjusted to read the differential absorbance, $A = A_L - A_R$. This quantity is related to the difference in molar absorptivity, $\epsilon = \epsilon_L - \epsilon_R$. Write down the equation that links A and ϵ . Give units for every quantity that occurs in this equation. Then explain what the “angle of ellipticity” is (an illustration would be better than a long epic description).

$A = f(\epsilon)$: (5 points)

The “angle of ellipticity”, θ , mmmh, let’s see ... (5 points)

Question 3. Absorbance Spectra and CD Cotton Effects. (20 points)

(a) Suppose you have a material that has an allowed electronic transition centered at a wavelength of $\lambda = 500$ nm. Draw schematic spectra as requested. In each case, the horizontal axis will be the wavelength axis and λ increases to the right (the usual convention). Assume that $\lambda = 500$ nm is just in the middle. For the vertical axis, provide the quantity that is being measured and indicate the sign (no need to give numbers and magnitudes, no need to give units). (3 points each box)

The UV/Vis spectrum of the pure <i>R</i> -enantiomer.	The CD spectrum of the pure <i>R</i> -enantiomer with <u>positive</u> Cotton effect (assumed in our case).
The UV/Vis spectrum of the pure <i>S</i> enantiomer.	The CD spectrum of the pure <i>S</i> -enantiomer.
The UV/Vis spectrum of the racemate.	The CD spectrum of the racemate.

Why is the Cotton effect called the “Cotton” effect? (2 points)

- ___ Named after F. Albert Cotton (the Cotton from the text Cotton & Wilkinson)
- ___ The effect was first discovered in studies of “cotton”, the plant.
- ___ Named after Aime Cotton, a French female physicist.
- ___ Named after Aime Cotton, a French male physicist.

Question 4. Exciton Coupling and Bisignate Cotton Effects. (20 points)

(a) If two chromophores X and Y have very similar absorption bands ($X = Y$ or $X \approx Y$) and if these two chromophores are in (relatively) close proximity (even 1000 pm can be close in this case), then the bichromophoric composite system will exhibit an exciton splitting (Davydov splitting). As the consequence of this interaction between the excited states, the one absorption (or the two almost identical absorptions) of the individual chromophores X and Y now will split into one transition at higher and one transition at lower energy. Draw a diagram that illustrates this situation. (5 points)

(b) What are the effects on the UV/Vis and the CD spectra? The UV/Vis band will _____ (narrow, broaden) compared to that of the band of X or Y alone. More change occurs in the CD spectrum since the signs of the Cotton effects of the two transitions will be opposite and a bisignate shape of the CD curve occurs. One speaks of “positive exciton chirality” if the Cotton effects at _____ (longer, shorter) wavelength is positive. (The exciton chirality can be related to absolute chirality via the so-called exciton chirality rules.) As with Question 3 (a), draw schematic spectra as requested. (15 points)

UV/Vis spectrum of one chromophore X:	UV/Vis spectrum of two exciton-coupled chromophores X:	CD spectrum of two exciton-coupled chromophores X with <u>positive</u> exciton chirality.
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Question 5. Exciton Coupled CD Spectra of Retinal and Derivatives. (50 points)

“Absolute Sense of Twist of the C12-C13 Bond of the Retinal Chromophore in Bovine Rhodopsin on Exciton-Coupled CD Spectra of 11,12-Dihydroretinal Analogues.” Qiang Tan, Jihong Lou, Babak Borhan, Elena Karnaukhova, Nina Berova, and Koji Nakanishi *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2089-2093.”

Figure 1 shows the structure of the 11-*cis*-retinal chromophore in native rhodopsin. The UV/Vis and CD spectra are shown of bovin rhodopsin in octylglucoside.

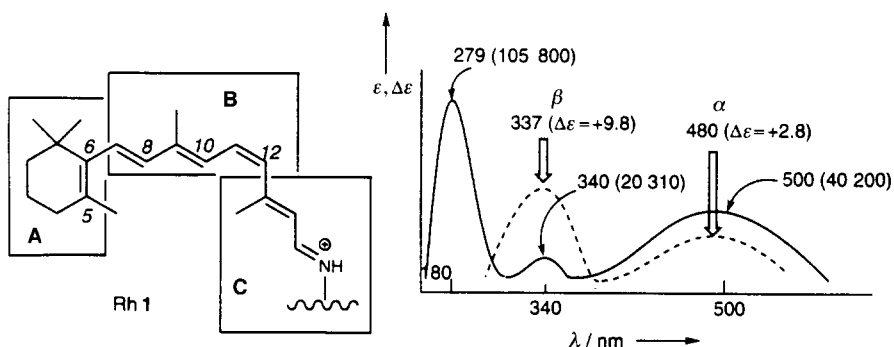


Figure 1. The 11-*cis*-retinal chromophore **1** in native rhodopsin attached in PSB form, and the UV/Vis (—, ϵ) and CD spectrum (---, $\Delta\epsilon$) of bovin rhodopsin in octyl glucoside.

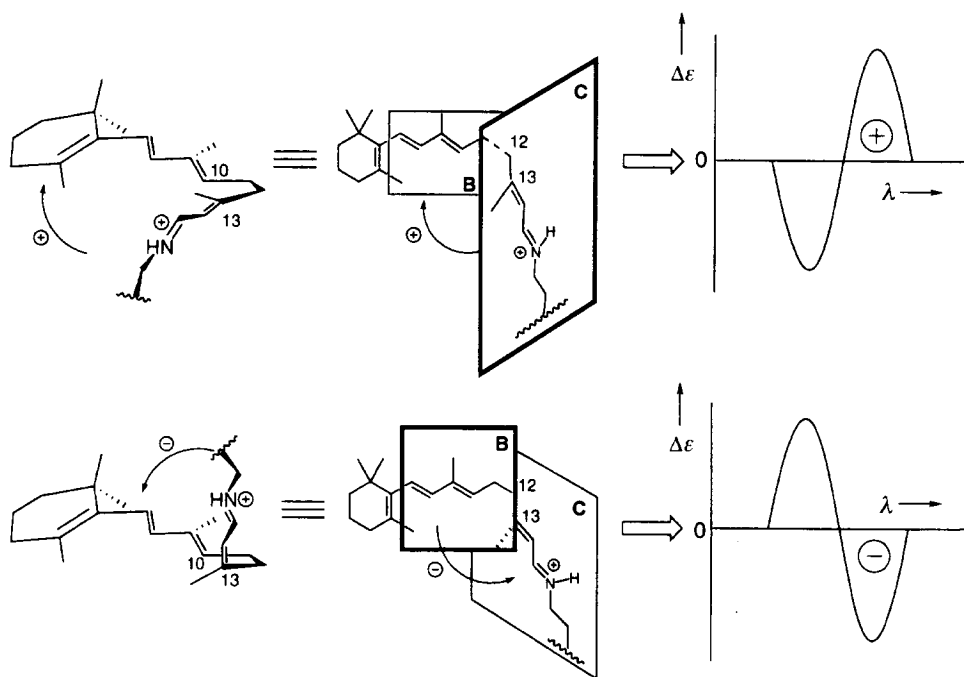
(a) Looking at the CD spectrum, one realizes that there are two bands that show Cotton effects: One band at _____ nm shows a _____ (positive, negative) Cotton effect and the other band at _____ nm shows a _____ (positive, negative) Cotton effect. The simple fact that bovin rhodopsin shows a CD spectrum indicates that the chromophore is _____ (chiral, achiral). Realize that there are _____ (give number) chirality centers in **A**, _____ (give number) chirality centers in **B**, and _____ (give number) chirality centers in **C**. (Ignore the attachment to the imine-*N*. Whatever chirality centers might be in there, they all are far away as far as the present discussion is concerned.) (8 points)

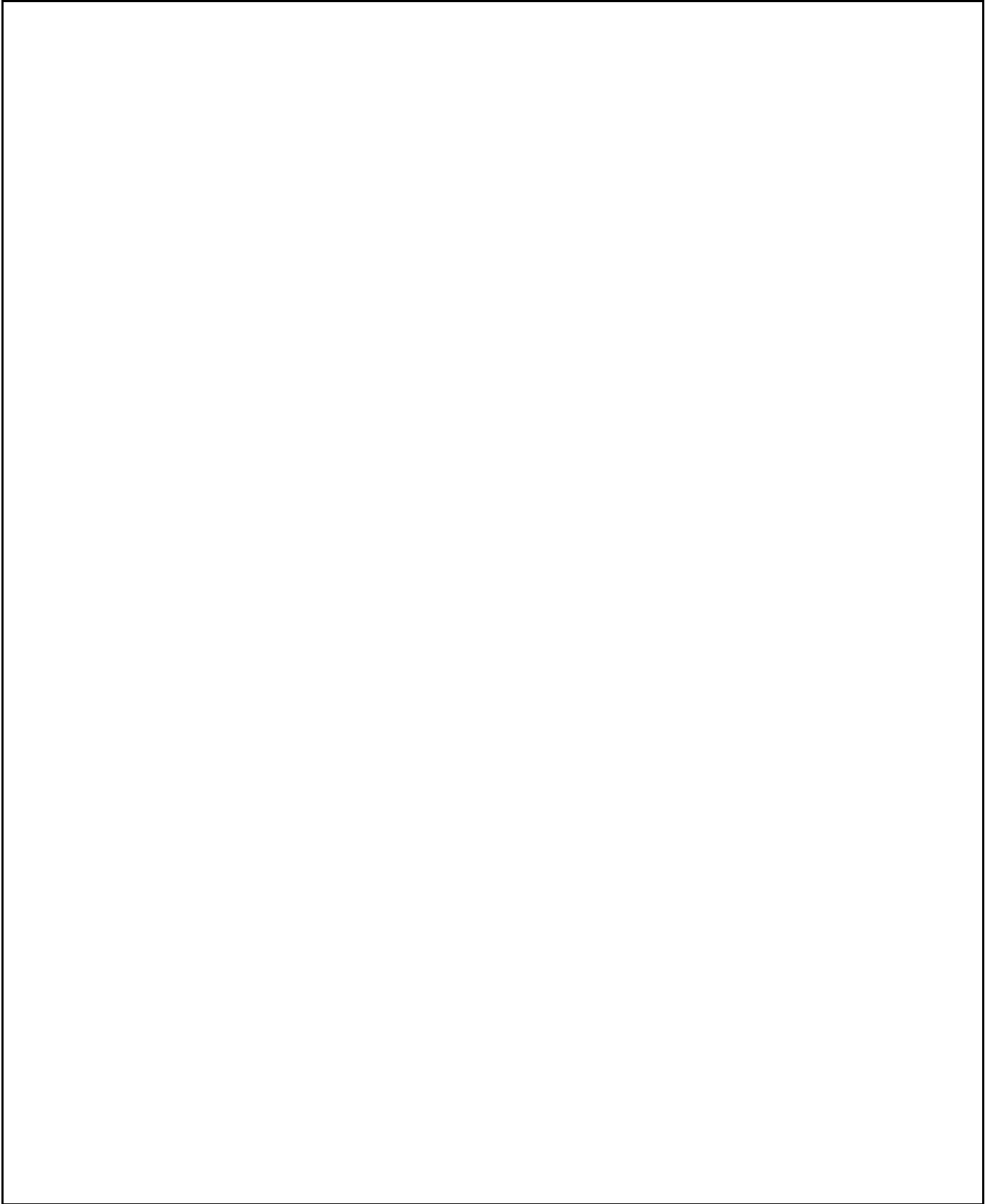
(b) Experiments show that the _____ band vanishes when planes **B** and **C** are forced to co-planarity. Experiments also show that the _____ band vanishes when planes **A** and **B** are forced to co-planarity. (6 pts)

Explain.

(c) Consider butadiene. Butadiene forms two stable conformers. The most stable conformation is _____ (*cis*, *trans*, *gauche*) and the other conformation is _____ (*cis*, *trans*, *gauche*). Considering this information, one might have expected that planes **A** and **B** _____ (are, are not) coplanar and that planes **B** and **C** _____ (are, are not) coplanar. (6 points)

(d) To determine the absolute direction of the twist around the C12-C13 bond, Nakanishi *et al.* wanted to “disrupt the conjugates polyene by a single bond so that the two polyene moieties flanking the single bond would couple. The sign of the resulting bisignate couplet would reflect the twist in a nonempirical manner.” This expectation was illustrated by the figure which is reproduced below without its caption. Explain this reasoning. State “what” is expected “to couple”. State why it is reasonable to expect such coupling. State why the drawn configurations are expected to give the bisignate spectra shown. For each of the spectra state whether they show positive or negative exciton chirality. Use precise language as much as possible. (20 points)





(e) Nakanishi *et al.* incorporated the (protonated Schiff base of the) 11,12-dihydroretinal into opsin and measured the CD spectrum. The triene absorbs at 255 nm. The protonated Schiff base absorbs at 270. The CD spectrum shows negative exciton coupling with a maximum at 275 nm and a minimum at 295 nm. Provided that 11,12-dihydroretinal adopts essentially the same conformation as that of 11-*cis*-retinal in rhodopsin, the exciton coupling allows one to deduce the absolute stereochemistry. Show the structure with the correct conformation and argue briefly for it. (10 points)

