

Chemistry 416 "Spectroscopy"  
Winter Semester 1996  
Dr. Rainer Glaser

First 1-Hour Examination  
"UV/Vis Spectroscopy"

Friday, February 9, 1996, 8:40 - 9:30

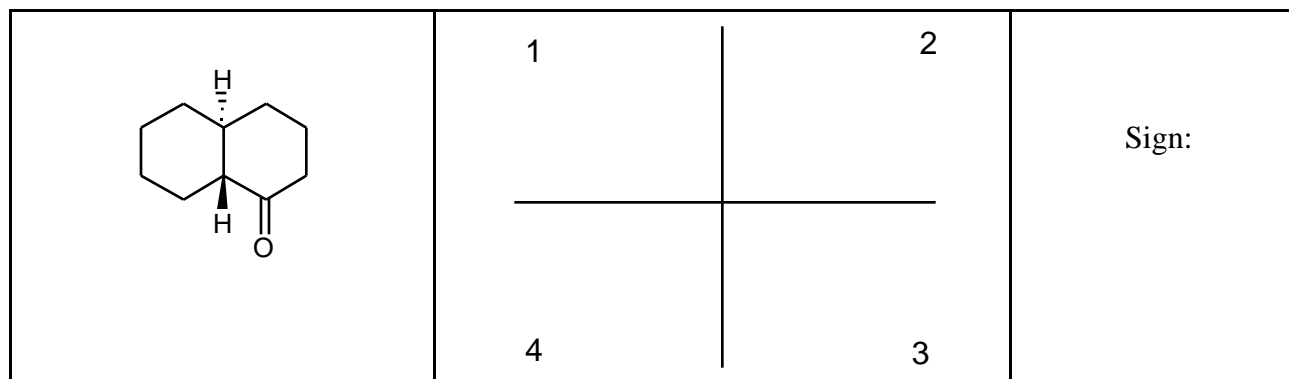
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|            | Max | Yours |      |
|------------|-----|-------|------|
| Question 1 | 10  |       |      |
| Question 2 | 10  |       |      |
| Question 3 | 20  |       |      |
| Question 4 | 10  |       |      |
| Total      | 50  |       | •2 = |

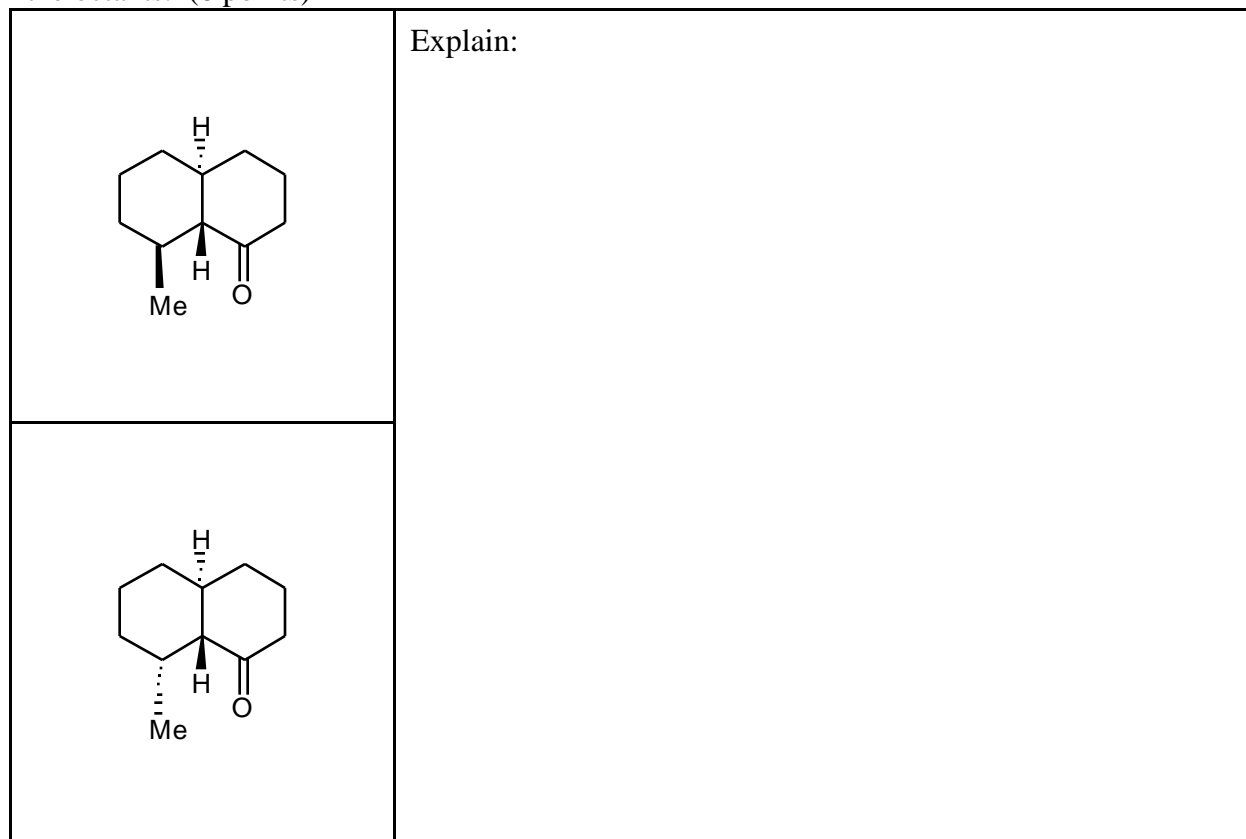
**Question 1. Octant Rule.** (10 points)

“The Chiroptical Properties of Carbonyl Compounds” D. N. Kirk *Tetrahedron* **1986**, *42*, 777.

(a) In the space provided in the center, draw the projection of ketone **1**. Indicate the sign for each of the quadrants in the drawing. Determine the overall sign for **1**. (4 points)



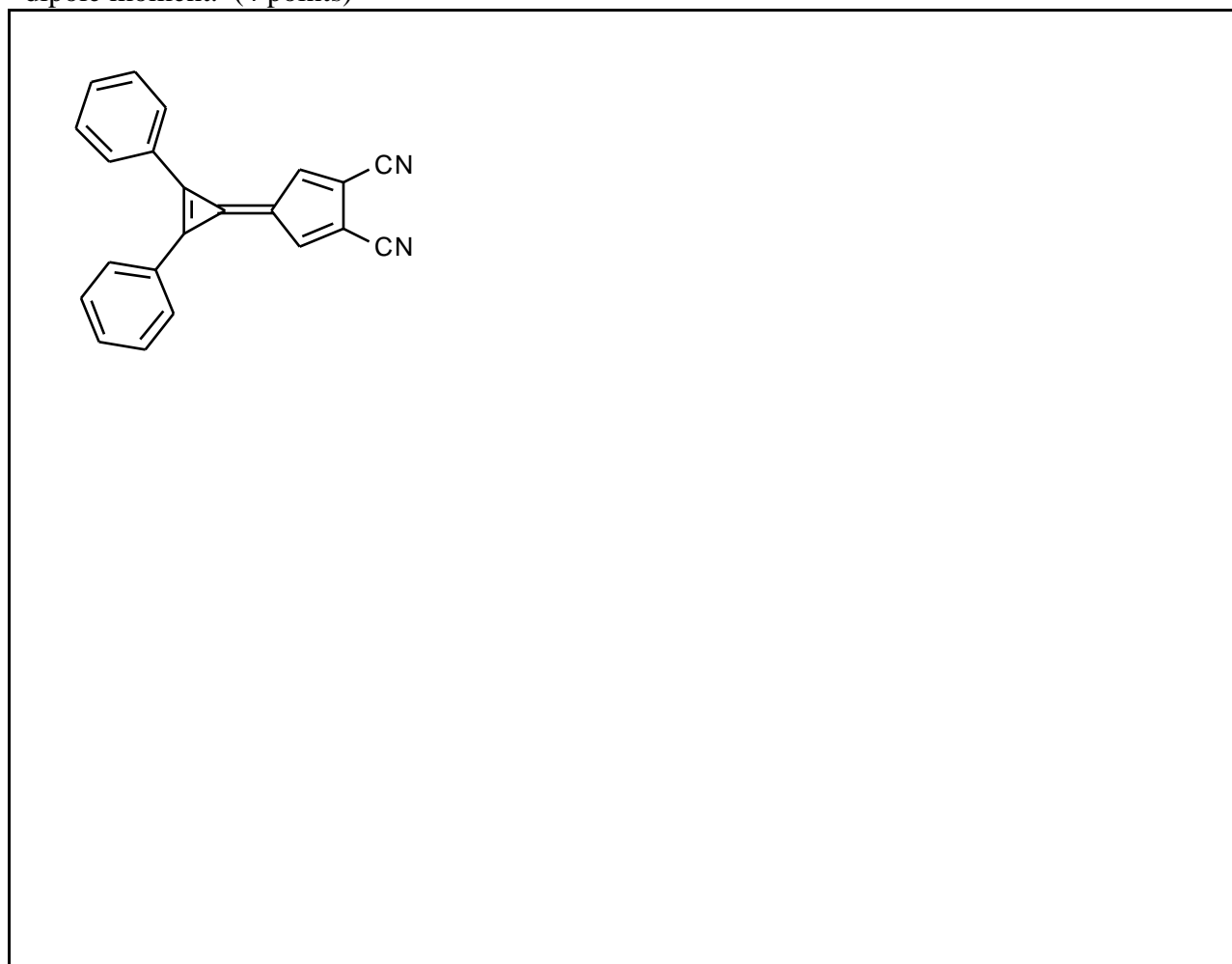
(b) Now consider the two derivatives with their methyl groups in the  $\alpha$ -position. Consider very carefully whether this methyl group lies in octant 1, octant 2, octant 3, or octant 4, or in neither one of these. Explain your answer with a drawing that clearly shows the three planes that define the octants. (6 points)



**Question 2. Solvent Effects.** (10 points)

“Solvents and Solvent Effects in Organic Chemistry” C. Reichardt, 2nd edition, Verlag Chemie, Weinheim, Germany, 1990, page 292.

(a) The molecule with the structure shown is quite polar. The dipole moment in the ground state is  $48 \cdot 10^{-30}$  Cm or 14.4 Debye! Using resonance forms, explain briefly the origin of this high dipole moment. (4 points)



(b) The molecule absorbs at  $27,250 \text{ cm}^{-1}$  when dissolved in cyclohexane. This transition is shifted by  $1,570 \text{ cm}^{-1}$  when the spectrum is recorded in acetonitrile solution. The peak will certainly undergo a \_\_\_\_\_ shift because the dipole moment in the \_\_\_\_\_ state is \_\_\_\_\_ compared to the ground state. Because of this \_\_\_\_\_ solvatochromism the peak occurs at \_\_\_\_\_  $\text{cm}^{-1}$  in acetonitrile. Clearly, solvation effects in the fluorescence spectrum would be \_\_\_\_\_ (more or less) than in the absorption spectrum. (6 points)

**Question 3. Circular Dichroism and Exciton Chirality Rule.** (20 points)

“A Chiroptical Method for Determining the Absolute Configuration of Allylic Alcohols.”

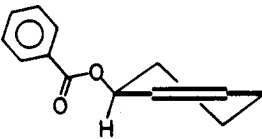
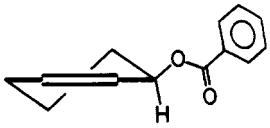
N. Harada, J. Iwabuchi, Y. Yokota, and H. Uda *J. Am. Chem. Soc.* **1981**, *103*, 5590.

The circular dichroic exciton chirality method, a nonempirical method based on the coupled oscillator theory, was successfully used in various organic compound for the determination of absolute configuration. As an extension of the exciton chirality method, these authors report a new CD method for determining absolute stereochemistries of allylic alcohols.

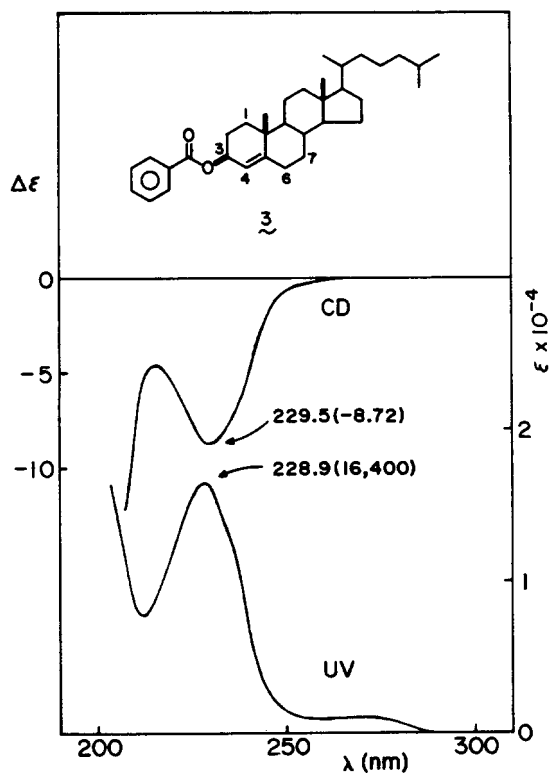
(a) Read along and fill in the appropriate answer or circle the correct choice. (8 pts, 2x2+4\*1)

The concept of chiral exciton coupling can be extended to nondegenerate systems which are composed of two different chromophores. Allylic benzoates give rise to a coupled nondegenerate system. Namely the benzoate chromophore exhibits an allowed \* charge transfer band at \_\_\_\_\_ nm, while the C=C double bond chromophore also shows an allowed \* transition around \_\_\_\_\_ nm. Both transitions are polarized along the long axis of each chromophore. If the two long axes of benzoate and double-bond chromophores constitute a positive exciton chirality (right-handed screwness), then the exciton chirality rule predicts that the first Cotton effect at \_\_\_\_\_ (longer/shorter) wavelength is \_\_\_\_\_ (positive/negative) and the second Cotton effect at \_\_\_\_\_ (longer/shorter) wavelength is \_\_\_\_\_ (positive/negative) and *vice versa*.

(b) Two enantiomers are shown of an allylic benzoate. Which one of these enantiomers exhibits “positive chirality”? For the enantiomer that does exhibit the positive chirality, indicate clearly whether you would expect a positive or negative Cotton effect for the benzoate chromophore. (4 points, 2 points each part if the answer is shown in conjunction with the correct structure).

|   |  |
|---|--|
| _____ chirality   | _____ chirality  |
|  |  |
| _____ benzoate Cotton effect  | _____ benzoate Cotton effect   |

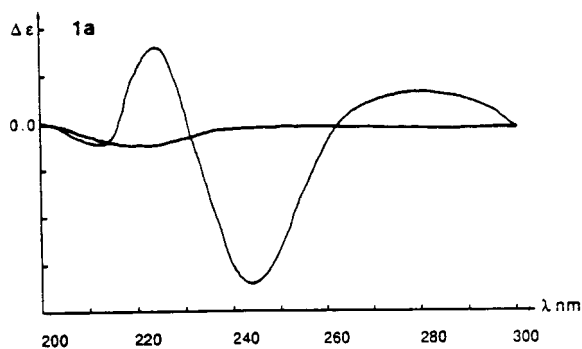
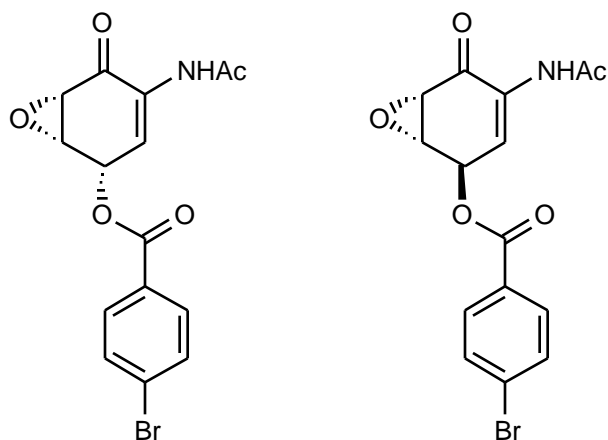
(c) The CD and UV spectra are shown of cholest-4-en-3-yl benzoate (**3**) in EtOH. From the spectrum it is obvious that the band at about 230 nm — this band is due to the \_\_\_\_\_ chromophore (1 point) — exhibits a \_\_\_\_\_ (1 point) Cotton effect. Consequently, **3** exhibits \_\_\_\_\_ (2 points) chirality. Therefore, the chirality of C3 in the R/S nomenclature is \_\_\_\_\_ (4 points). (Total points: 8 points).



**Question 4. Circular Dichroism and Exciton Chirality Rule.** (10 points)

“Structure and Absolute Stereochemistry of the Epoxyquinol LL-C10037 and Related Metabolites from *Streptomyces* LL-C10037.”

B. Shen, Y. G. Whittle, S. J. Gould, and D. A. Keszler *J. Org. Chem.* **1990**, *55*, 4422.



CD spectrum in MeOH

The CD spectrum of the pure enantiomer shows a split Cotton effect which is due to the interaction between the benzoate chromophore and the enone chromophore. Indicate in the spectrum which peak belongs to which chromophore. Applying the exciton chirality rule, the first \_\_\_\_\_ Cotton effect corresponds to a \_\_\_\_\_ chirality and the projection between the two chromophores should be \_\_\_\_\_ (counterclockwise or clockwise). Circle the enantiomer that gives rise to the spectrum shown. (2 point each written answer and 4 points for the selection of the correct enantiomer)

The End of an Another Exciting Learning Experience - Relax.