

Chemistry 416 "Spectroscopy"  
Fall Semester 1993  
Dr. Rainer Glaser

First 1-Hour Examination  
"UV/Vis Spectroscopy"

Friday, September 17, 1993, 8:40 - 9:30

Name:
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Question 1	20	
Question 2	24	
Question 3	16	
Question 4	10	
Question 5	12	
Question 6	18	
Total		

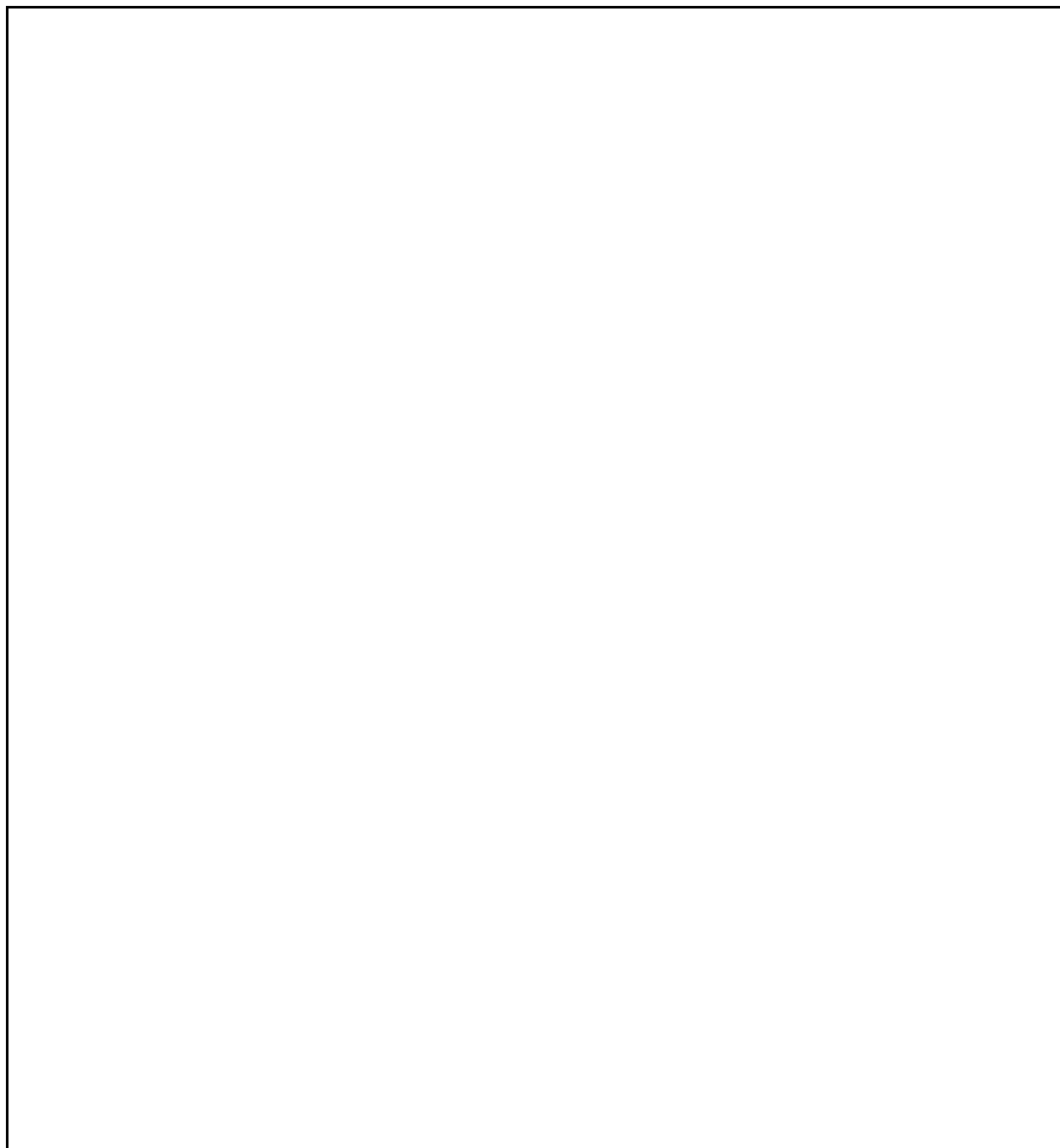
**Question 1. Polyenes and MO Diagrams.**

(a) Draw all 4  $\pi$ -MOs of butadiene schematically, that is, the two occupied and the two unoccupied MOs. Then draw MO level diagrams for the ground state, the first excited singlet state, the second excited singlet state, and for the lowest excited triplet state. Clearly show the electron occupation using up and down arrows to indicate spin. (20 p)

The MOs (4 points):

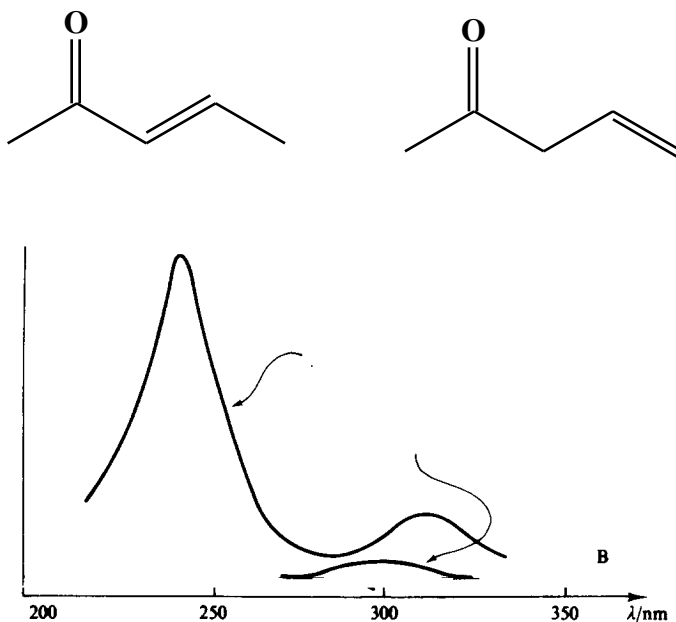
The MO level diagrams (8 points):

(b) Draw a schematic diagram that shows the relative energy of these four states of butadiene. The vertical axis is the energy axis. Indicate with an arrow the excitation that corresponds to the lowest energy absorption. Indicate with an arrow the lowest energy fluorescence emission. Indicate with an arrow the lowest energy phosphorescence emission. Also indicate the intersystem crossing via an arrow. Label each arrow in your drawing! (8 points)



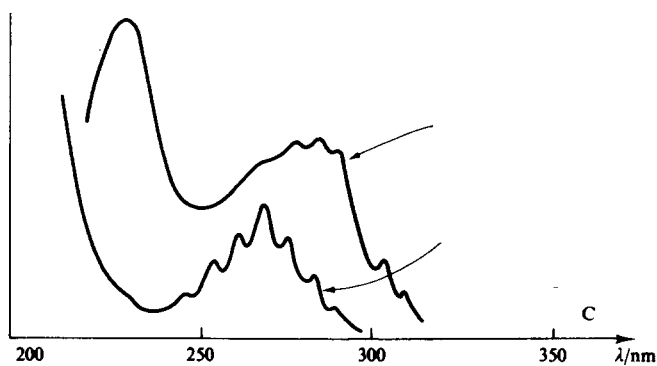
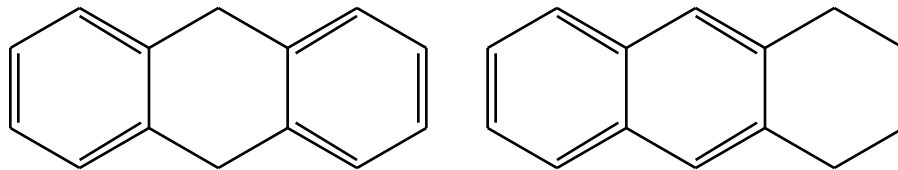
**Question 2. Some Qualitative Applications of UV/Vis Spectroscopy.**

(a) The spectra are shown of the two isomeric ketones. The x-axis shows the wave length increasing to the right. Assign the correct spectrum to each ketone. What types of transitions do these bands correspond to? Give approximate estimates of the wave lengths at which these absorptions occur (in nm). (6 points, Kemp 246)



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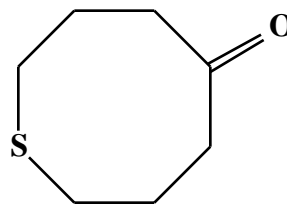
(b) You reduced anthracene by adding two Hs to it. Two of the possible products and their spectra are shown. Assign the isomers to the spectra. Explain your answer briefly. Circle that isomer which is the thermodynamically more stable one. (6 points, Kemp p. 246)



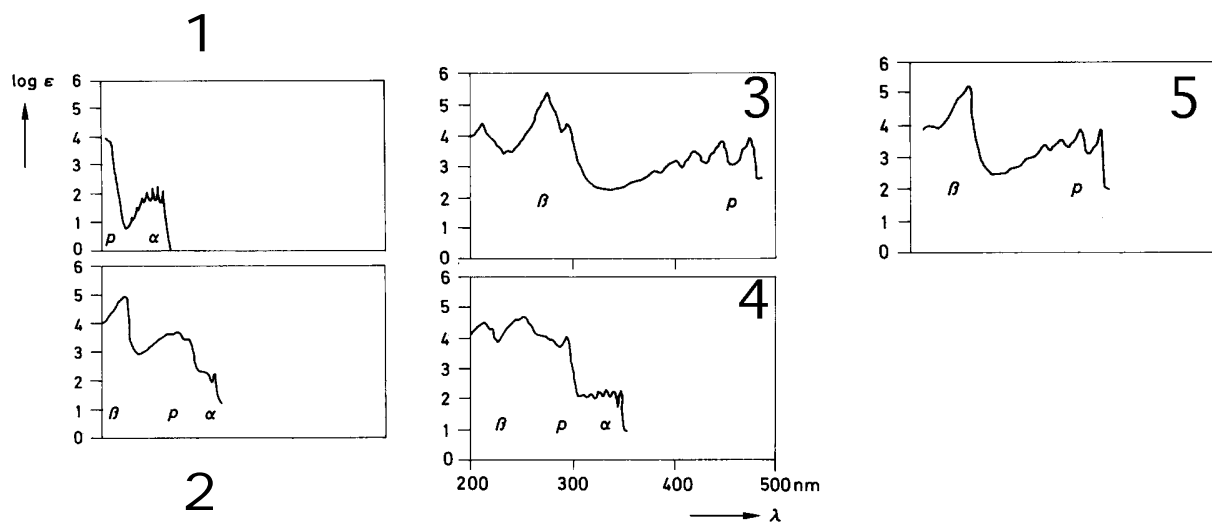
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(c) Pyridine shows an electronic transition at 257 nm because of the \_\_\_\_\_ excitation. In 2-hydroxypyridine and 4-hydroxypyridine, this band is shifted to 230 and 239 nm, respectively. What could have happened to cause this shift? (6 points, Silverstein p. 313)

(d) A normal saturated ketone shows an n \* band at about \_\_\_\_\_ nm. For the cyclic ketone shown, we observe a transition at 238 nm. What might cause this strong \_\_\_\_\_ (batho- or hypsochromic) shift? Draw structures that clearly show the 3-dimensional structure of the ketone. (6 pts, Silverstein, p. 304)



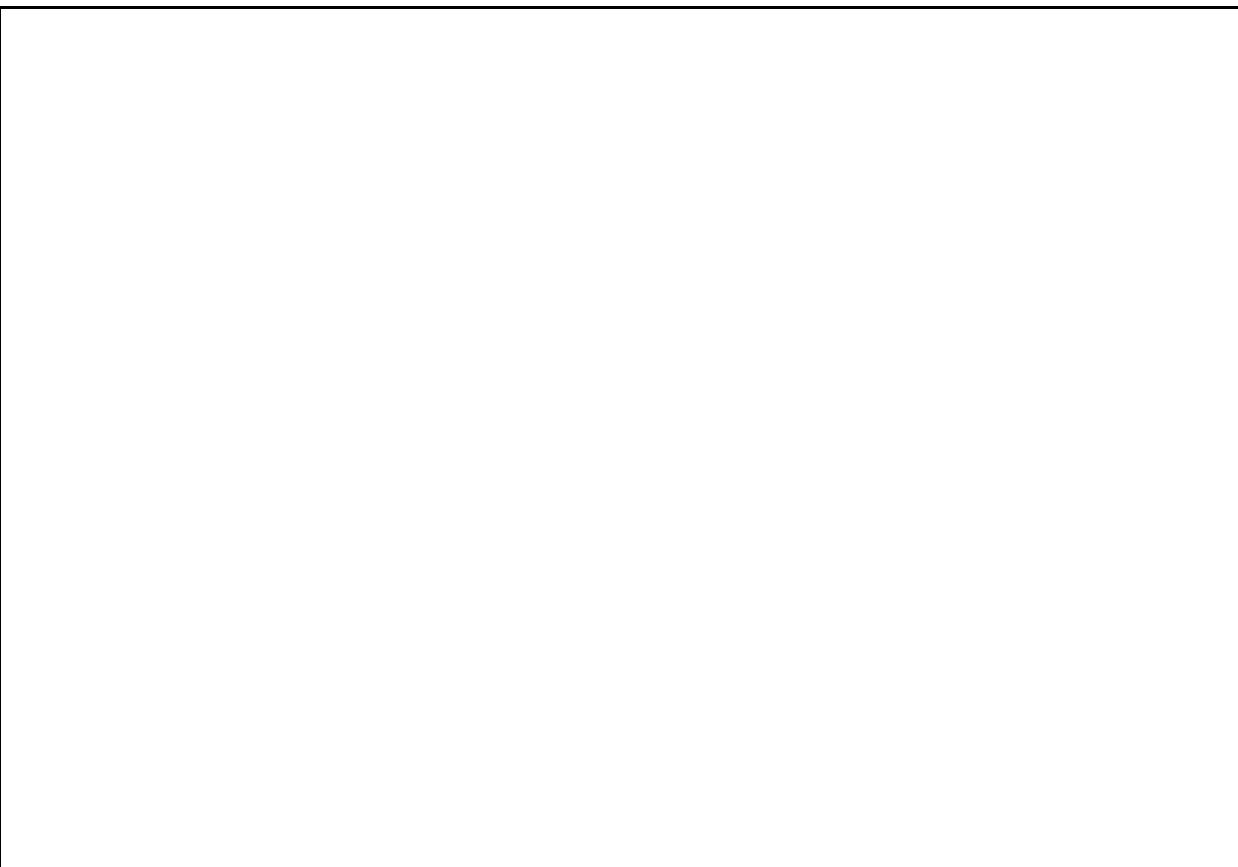
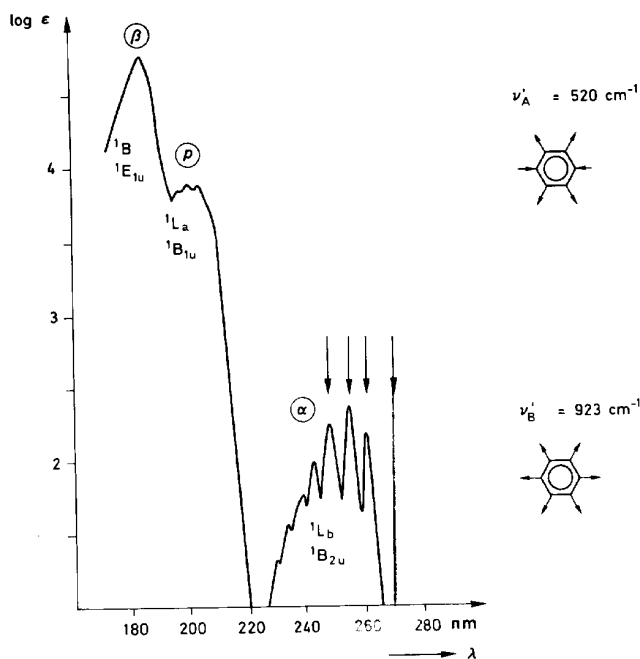
**Question 3. Aromatic Compounds and Franck Condon Factor.**



(a) The five spectra shown above are those of benzene, naphthalene, phenanthrene, anthracene, and teracene. Assign the appropriate compound to each of these spectra. Explain your assignment briefly. Explain in particular how you differentiate between the constitution isomers anthracene and phenantrene. (7 points)

(b) While benzene, naphthalene, and anthracene all are colorless, the tetracene is orange-yellow. What color is the light *absorbed* by tetracene? \_\_\_\_\_ (1 p)

(c) The spectrum of benzene is shown in more detail. Focus on the fine structure of the band designated as  $\alpha$  or  ${}^1L_b$ . Explain the fine structure using schematic drawings of the ground and excited state potential energy diagrams. For each band give the vibrational quantum numbers ( $v$  for ground state and  $v'$  for excited state) associated with it. **Note** that the  $v=0 \quad v'=0$  band does not show in the spectrum! (8 points)

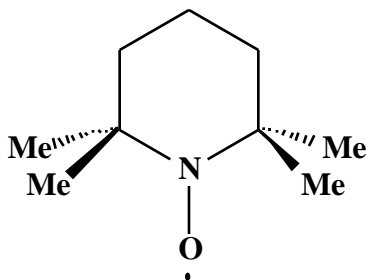




#### Question 4. Solvent Effects.

2,2,6,6-tetramethylpiperidine-1-oxyl radical exhibits a large \_\_\_\_\_ (negative or positive) solvatochromism of the weak \_\_\_\_\_ band while the intense \_\_\_\_\_ transition in the UV region is not sensitive to solvent changes. (3 points)

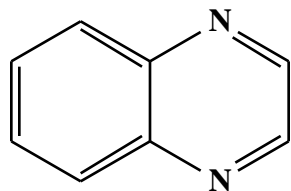
Fill in the “blanks” and explain the large solvatochromism observed. Use the correct terms and use resonance forms as necessary. (7 points, Reichardt, page 305.)



Solvent	n-hexane	acetonitrile	methanol	water
max	477	461	446	424

### Question 5. Solvent Effects.

The spectrum is shown of quinoxaline in *n*-heptane and in water. Focus your attention to the 340-400 nm region of this spectrum. The spectrum in that region is shown in more detail as a function of concentration of *iso*-propanol in hexane.



quinoxaline

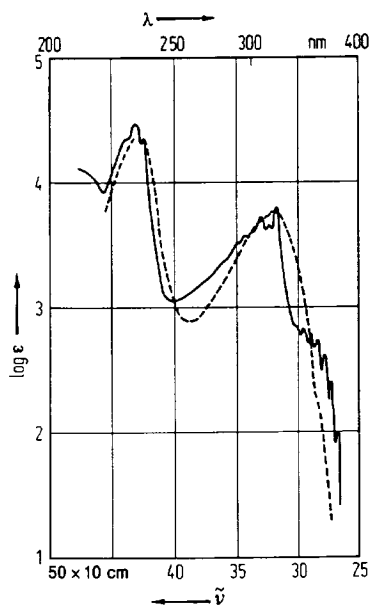


Fig. 55. Absorption spectrum of quinoxaline. *n*-heptane (—),  $\text{H}_2\text{O}$  (---)

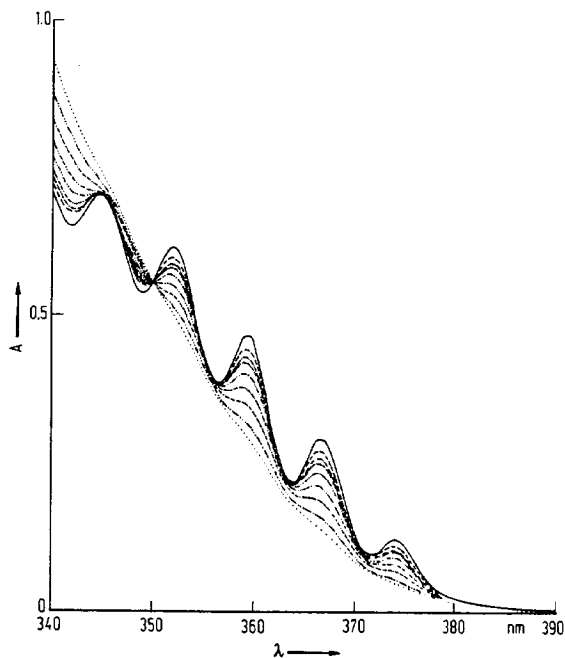


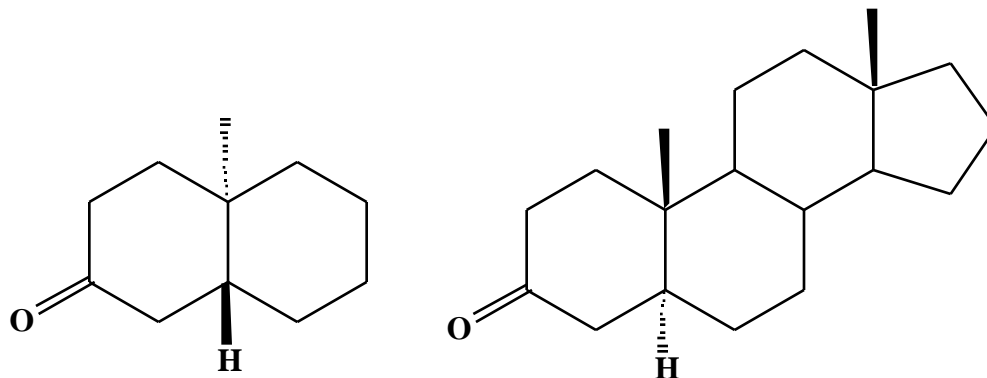
Fig. 56.  $n-\pi^*$  band of quinoxaline in *iso*-propanol/*n*-heptane mixtures as a function of the concentration of *iso*-propanol (full line, *n*-heptane; dotted lines, increasing concentration of *iso*-propanol)

(a) What type of excitation are we seeing here? What kind of solvent shift occurs (use the correct term) and explain why that shift occurs in that direction. Why does the vibrational structure disappear? (8 points)

(b) Explain with structural formulas what happens when the concentration of *iso*-propanol increases. (4 points)

### Question 6. Chircular Dichroism.

*Trans*-9-methyl-3-decalone with the absolute configuration shown displays a Cotton effect because the carbonyl chromophore is in a chiral environment. (a) Use the octant rule to determine the sign of this Cotton effect. (b) The steroid shown on the right also shows a Cotton effect. What is the sign of this Cotton effect. In this case, determine the sign by comparison to the decalone. Explain briefly. (18 points)



(a) Sign	Explain
(b) Sign	Explain

