CHEM6394: Stereochemistry — First Midterm Exam

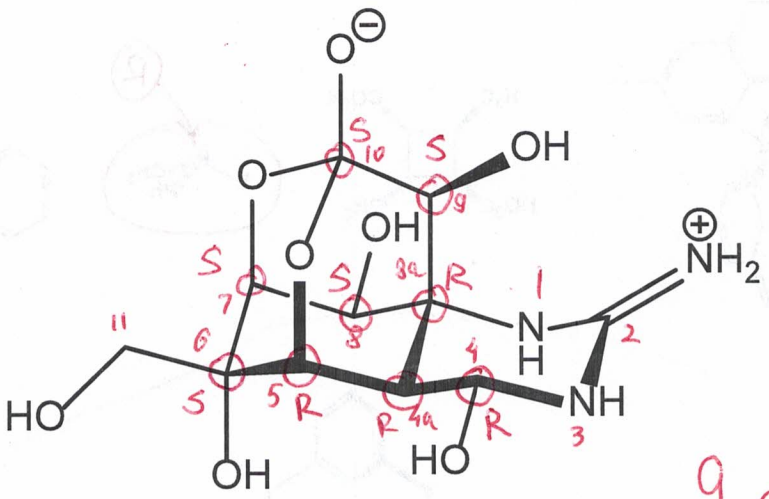
Prof. Ognjen Š. Miljanić — February 17, 2022

Name: Answer Key (print legibly) Last First — Last 4 Digits of Student ID Number: N/A

Read all directions very carefully. Write your answer legibly in the designated spaces. Total number of points is 200. This exam is supposed to have six (6) pages, with the last page intentionally left blank.

40

1. Tetrodotoxin is a potent neurotoxin, found in a number of marine species including pufferfish—even though it is actually produced by bacteria living symbiotically with the fish. How many chiral centers are there in the molecule of tetrodotoxin, shown below? Clearly mark all the chiral centers. Then, pick your favorite four and assign their configurations as (*R*) or (*S*). For the first stereospecific total synthesis of tetrodotoxin, see: Isobe et al. *J. Am. Chem. Soc.* **2003**, *125*, 8798–8805. *40 points*



tetrodotoxin

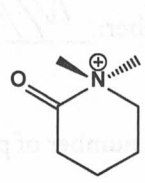
9 stereocenters

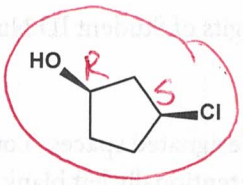
DO NOT WRITE IN THIS SPACE

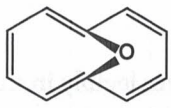
FINAL SCORE

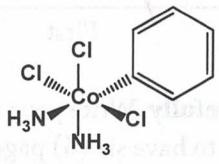
60

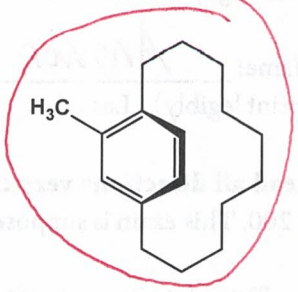
2. Circle all molecules that are chiral. For each chiral molecule, assign the configuration of its chiral elements with appropriate *R*/*S*, *A*/*C*, *M*/*P*, or Δ/Λ designators. *60 points*



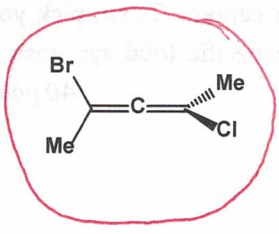


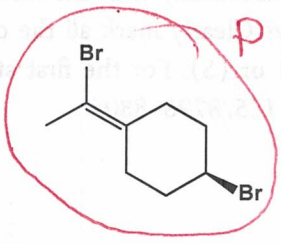




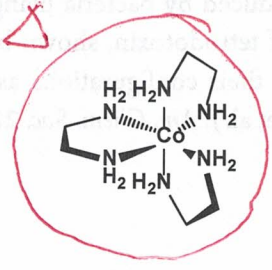


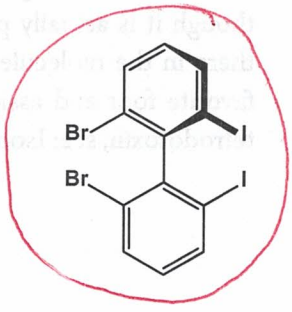
P

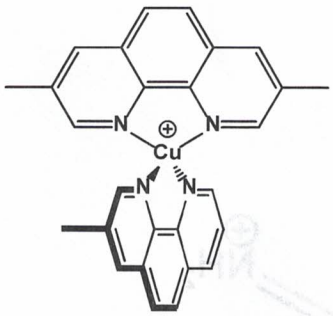


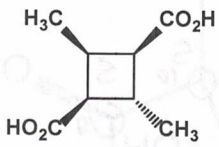


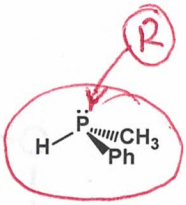
Δ

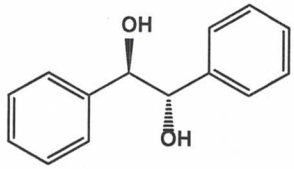


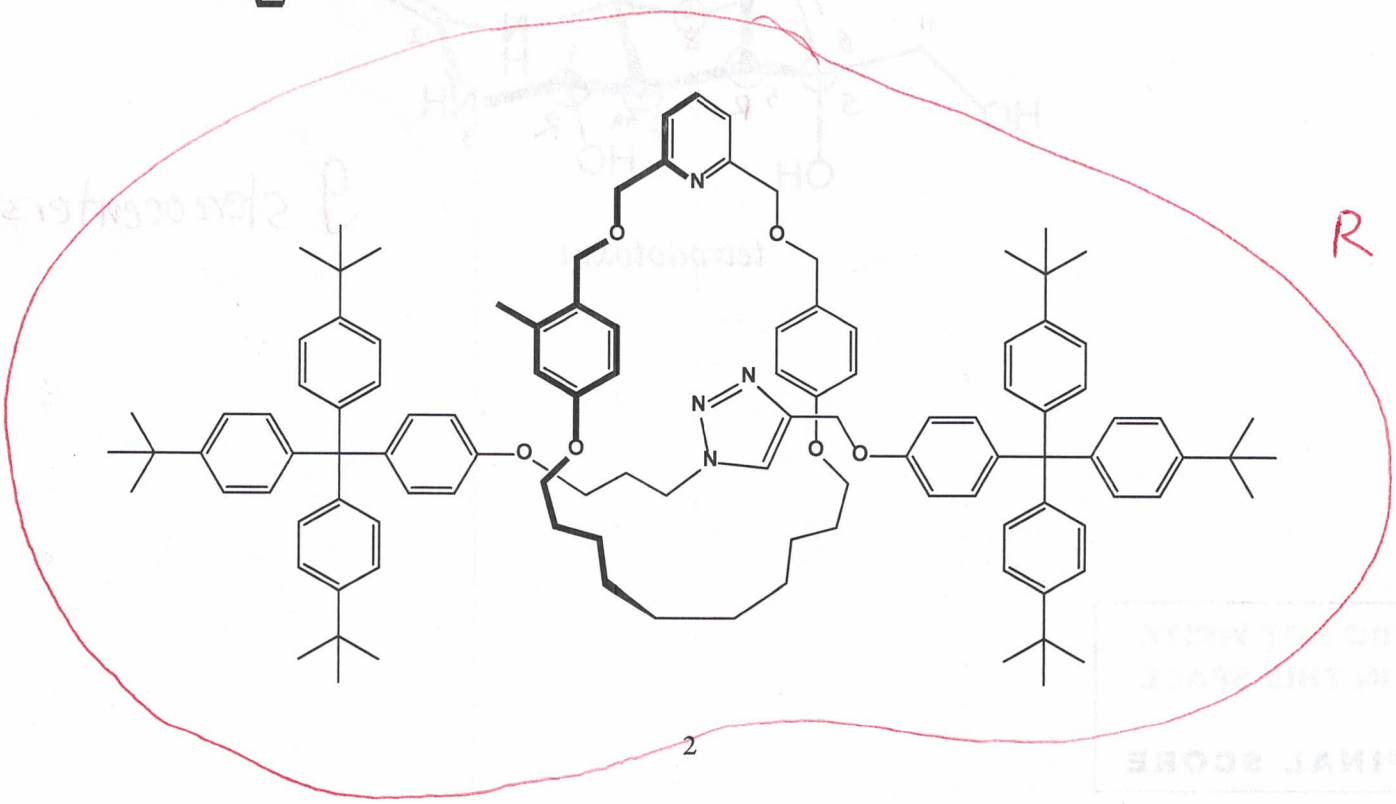












40

3. Natural honey is a mixture of glucose, fructose, and water, and its optical rotation is often use to determine its composition and purity. If a sample of honey has a water content of 16%, and a specific rotation of $[\alpha]_D^{20} = -14.8°\ dm^{-1}\ cm^3\ g^{-1}$, calculate the percentages of glucose and fructose in it. Specific rotation of glucose is $[\alpha]_D^{20} = +52.7°\ dm^{-1}\ cm^3\ g^{-1}$, and that of fructose is $[\alpha]_D^{20} = -92.0°\ dm^{-1}\ cm^3\ g^{-1}$. Assume that there are no other components in honey, and that the densities of honey, glucose, and fructose are the same. *40 points*

The honey sample is 84% mixture of glucose and fructose, and 16% water. If it were anhydrous, its specific optical rotation would have been:

$$\frac{100\%}{84\%} \times (-14.8\ dm^{-1}\ cm^3\ g^{-1}) = -17.6\ dm^{-1}\ cm^3\ g^{-1}$$

This rotation is a combination of rotations of glucose and fructose:

$$+52.7\,G - 92.0\,F = -17.6$$

Since there is no other components, $G + F = 100\%$ (or 1)

$$\left.\begin{aligned} &+52.7G - 92.0F = -17.6 \\ &G + F = 1 \\ &G = 1 - F \end{aligned}\right\} \quad +52.7(1-F) - 92.0F = -17.6$$

$$+52.7 - 52.7F - 92.0F = -17.6$$

$$+52.7 + 17.6 = 92.0F + 52.7F$$

$$+70.3 = 144.7F \rightarrow F = \frac{70.3}{144.7}$$

$$F = 0.486,\ 48.6\%$$

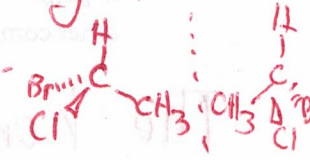
$$G = 1 - F$$

$$G = 51.4\%$$

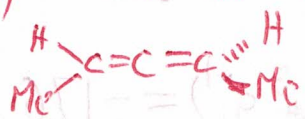
20

4. Define, in your own words, the following terms. Be succinct but precise, and feel free to use chemical structures to illustrate your definitions. *4 × 5 = 20 points*

Enantiomer is an isomer which relates to the original molecule as a non-superimposable mirror image.



Allene is an organic compound with two C=C double bonds immediately next to each other. Allenes are often axially chiral:

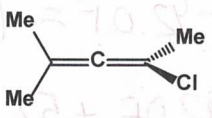


Axial ligand(s)

Planar chirality

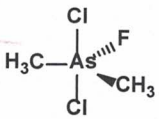
40

5. Which point groups do the following molecules belong to? *40 points*

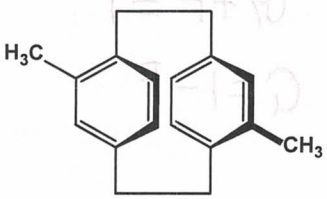


C_s

O_h



C_{2v}



C_i

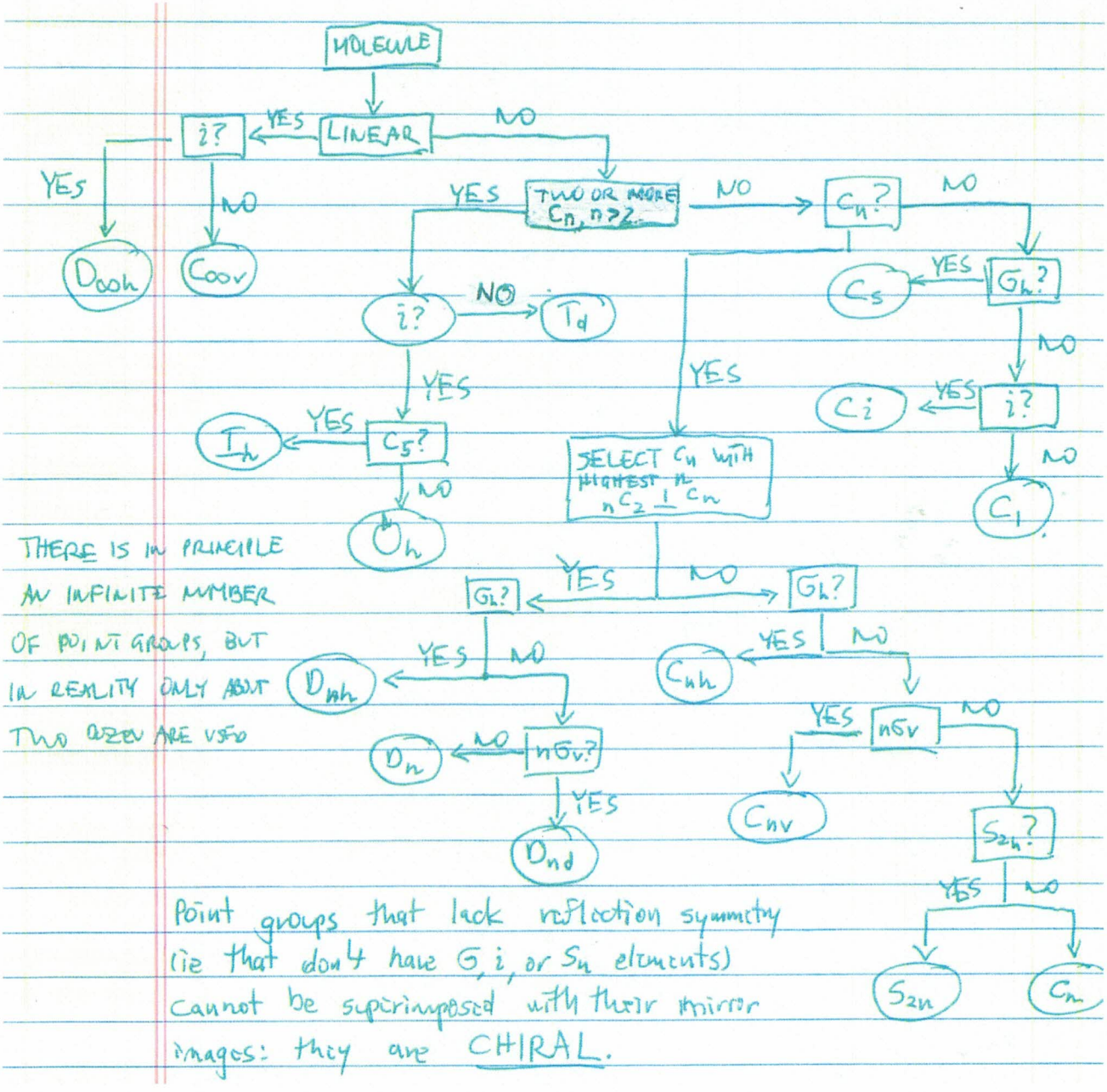



Chart for the Determination of Point Groups