 Name Key

Biochemistry 5700
Fall, 2005
Exam 2
October 4, 2004

INSTRUCTIONS:

Do not begin until 10:30 AM. The exam must be turned in by 11:20 AM. This exam should have 9 questions and 9 pages. Answer **all** questions completely, concisely, and legibly in the spaces provided. Good Luck!!

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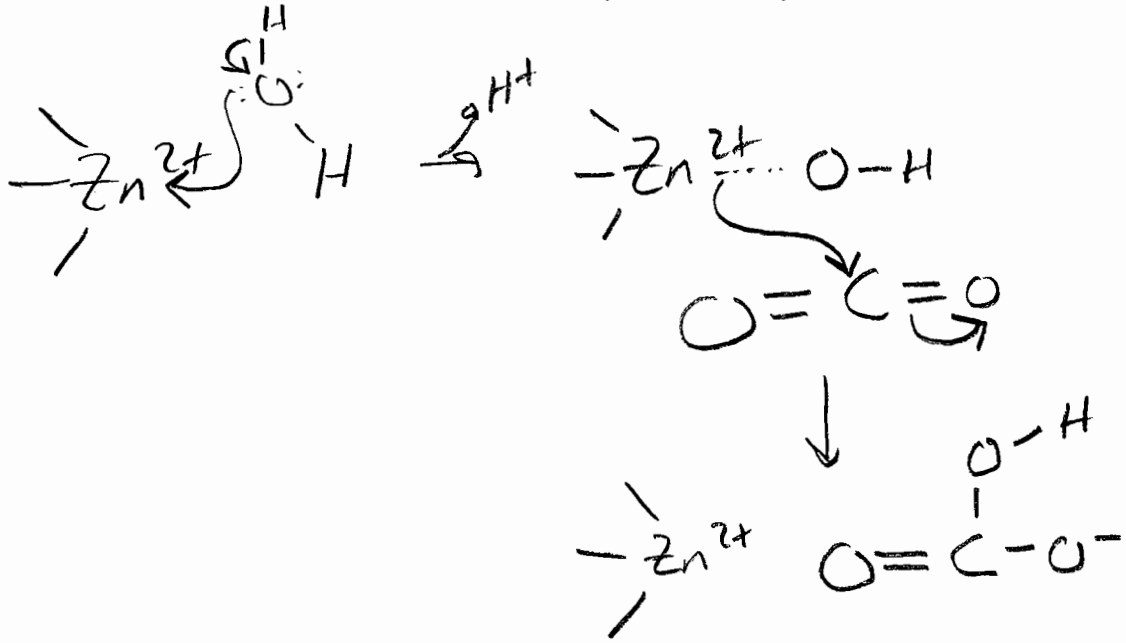
(1) (6 points) Carbonic anhydrase, a zinc-metalloprotein, catalyzes the reversible hydration of CO_2 to bicarbonate:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

Draw the reaction mechanism for carbonic anhydrase. Clearly show how Zn^{2+} facilitates catalysis.



(2) (3 points). For metal ion catalysis in general , what is the difference between charge shielding and charge stabilization?

In charge shielding a preexisting charge on a substrate is shielded by a metal ion to make an electrophile more reactive. In charge stabilization, a metal ion stabilizes a charge that develops on an intermediate or TS during catalysis

(3) (3 points) Briefly describe what a Schiff base adduct is and how it functions to accelerate a reaction.

A cationic imine formed from reaction between a primary amine and ketone or aldehyde. Provides an electron sink to stabilize a carbanion formed on a carbon α to the cationic imine C

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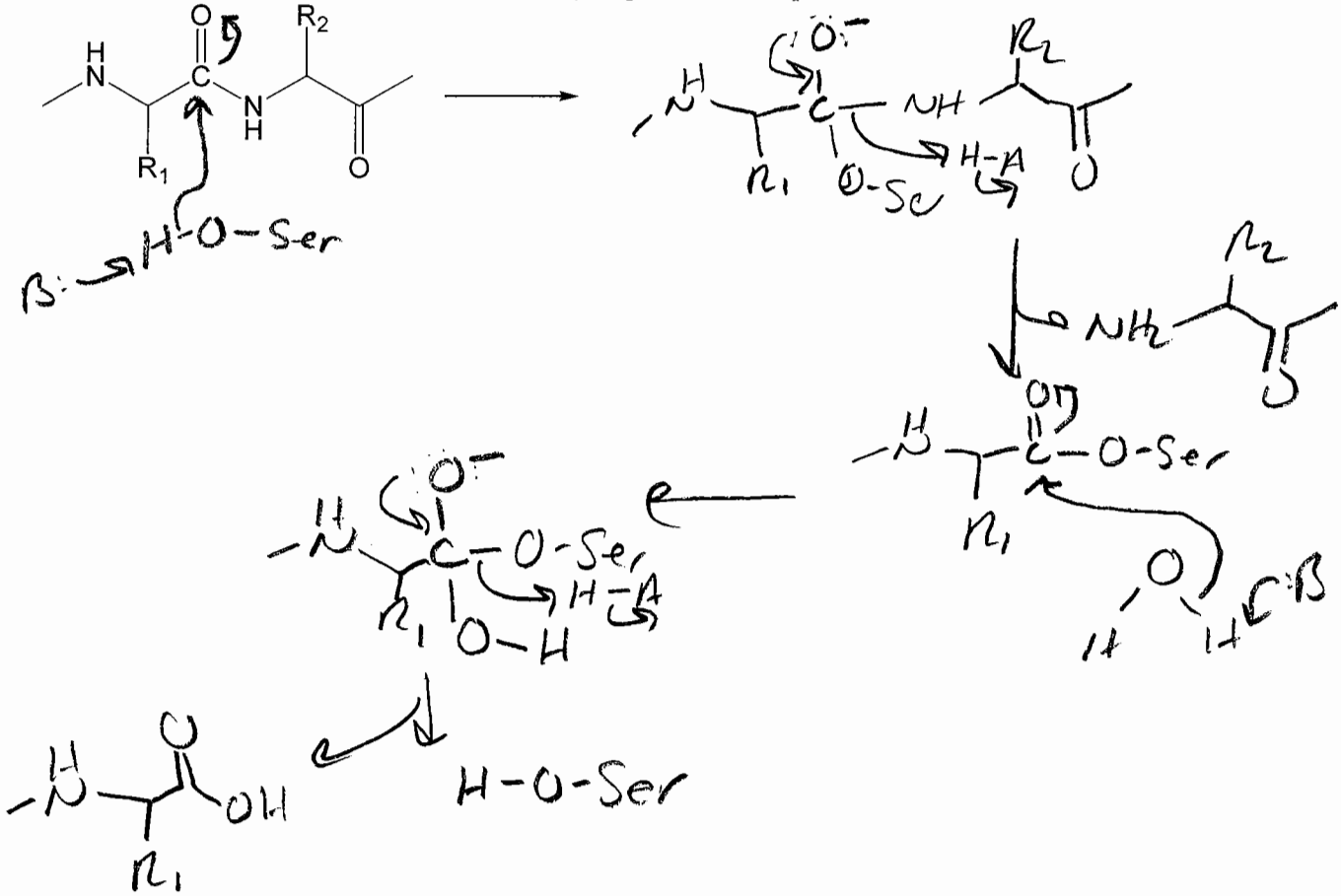
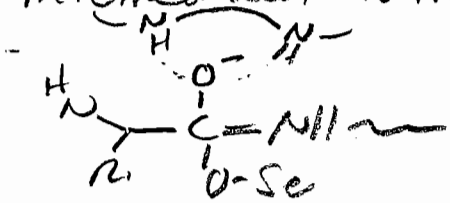
(4) (a) (8 points) Draw a complete reaction mechanism for chymotrypsin starting with the substrate shown below. Add all necessary electron pushing arrows and general acids/bases (you may abbreviate bases as "B" and acids as "HA") required to complete the mechanism.



(b) (6 points) Briefly describe the functions of the following features of chymotrypsin in accelerating the rate of the reaction. Feel free to use diagram(s) in answering the questions

(i) oxyanion hole

Stabilize 2 tetrahedral intermediates formed in catalysis



(ii) catalytic triad

lone pair of Ser so it can function as nucleophile at phys. pH, also provide general acid/base in 4 steps (histidine)

(iii) hydrophobic pocket

impart substrate specificity for aromatic AA residues at "R_1"

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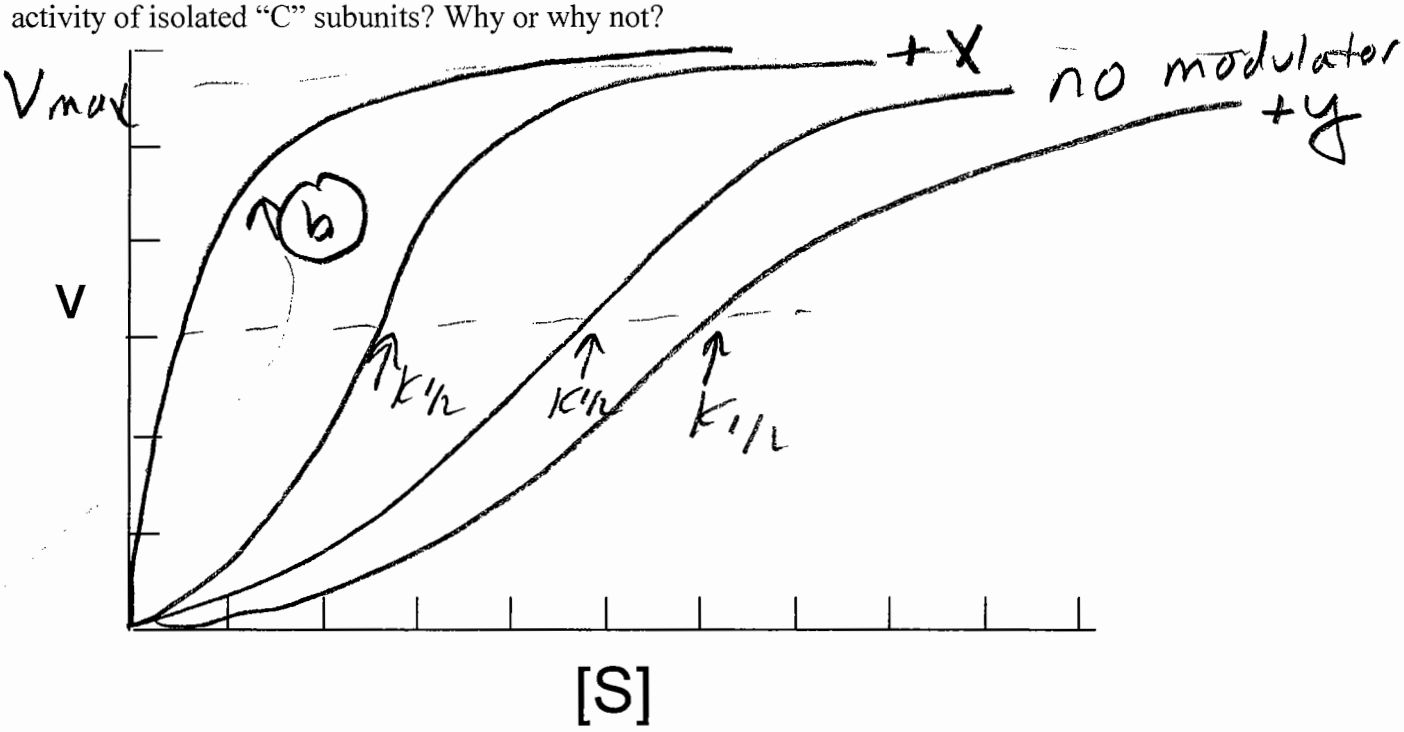
(5) Many allosteric enzymes have a C_nR_n quaternary structure (C stands for catalytic subunit, R for regulatory, where heterotropic modulaters bind to the "R" subunits). Suppose you have such an allosteric enzyme with subunit composition C_6R_6 for which molecule "X" is a positive heterotropic modulator and molecule "Y" is a negative heterotropic modulator. Both modulators perturb $K_{1/2}$ but not V_{max}.

(a) (6 points) Draw and label the kinetic plots that would be observed for the enzyme in the absence of modulator, in the presence of "X", and in the presence of "Y". Label the positions of V_{max} and $K_{1/2}$ for each line.

(b) (2 points) Assume that you are able to dissociate your enzyme into individual subunits, and that monomeric "C" subunits alone are catalytically active. On the plot, sketch what you would expect the v vs. S plot to look like for individual "C" subunits. Would you expect "X" or "Y" to affect the activity of isolated "C" subunits? Why or why not?



(b) no allostery expected, see normal M-M kinetics. X and y would not affect activity as they interact on subunit "R"

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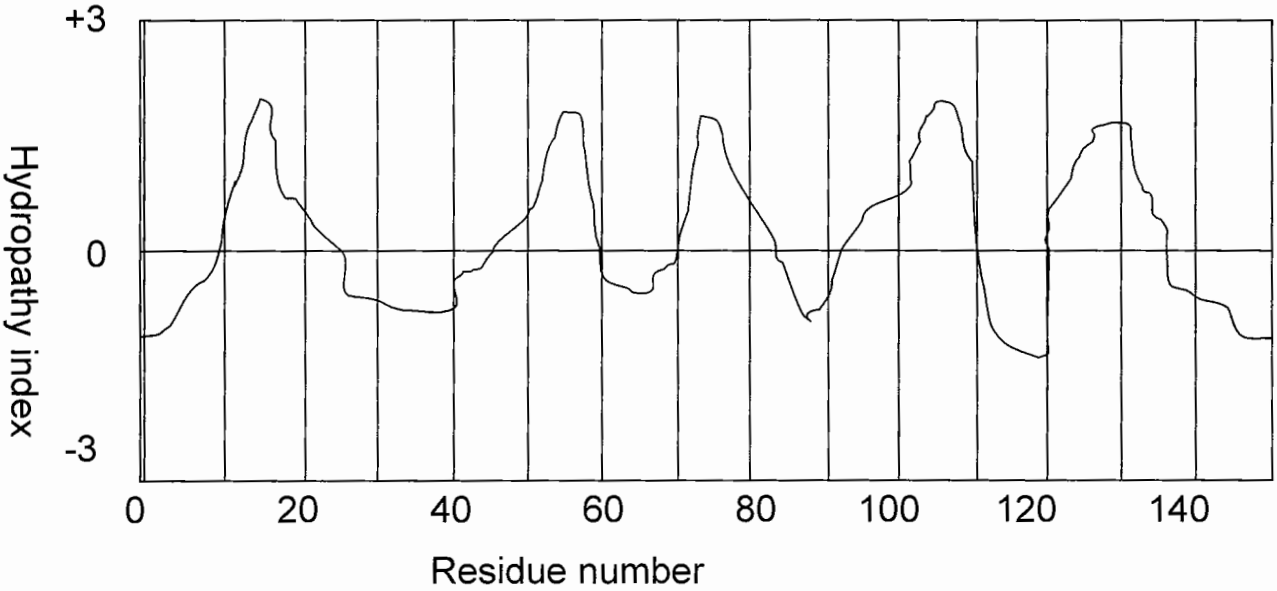
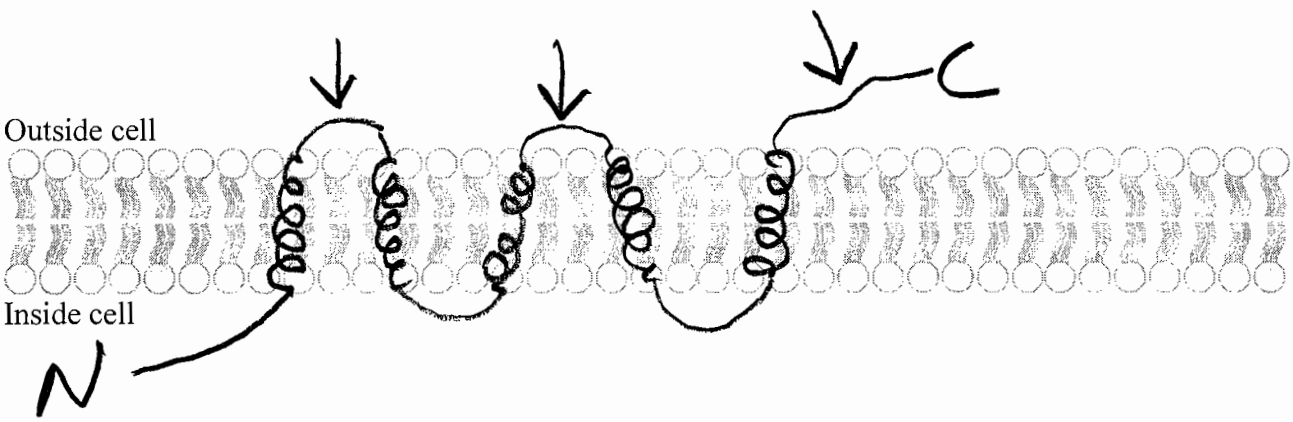
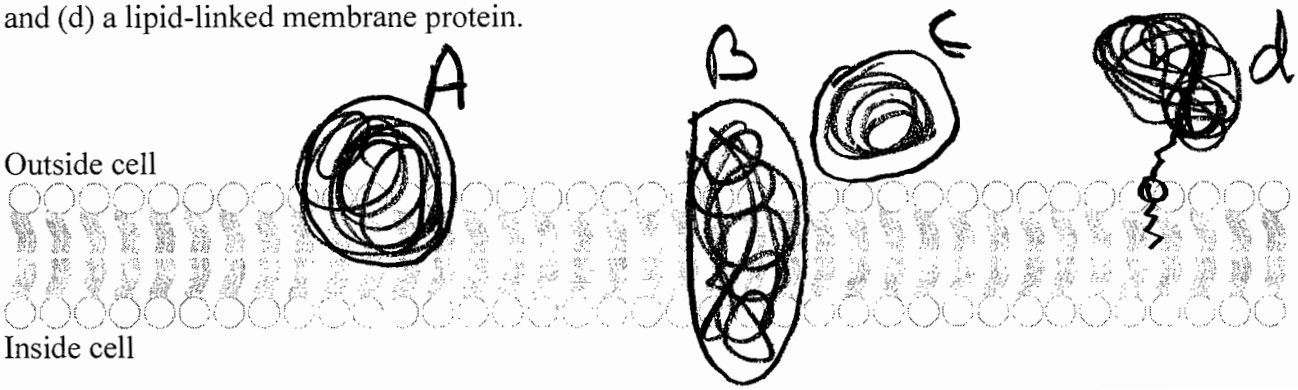
(6) Shown below is the hydropathy plot for a membrane protein. The N-terminus of the enzyme is known to be <u>inside</u> the cell.



(a) (5 pts) Diagram your protein on the lipid bilayer template provided below. Clearly indicate the N- and C-terminus of your protein on the diagram and clearly show each transmembrane spanning domain and the loops connecting them. With arrows, indicate portion(s) of your polypeptide that might be glycosylated.



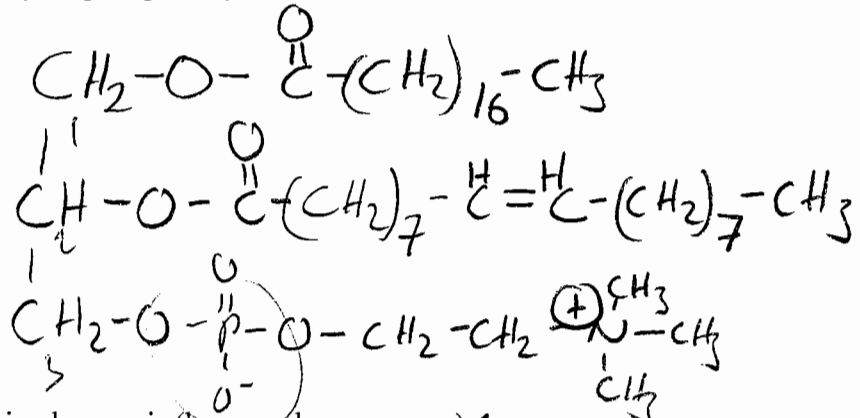
(b) (8 pts) On the lipid bilayer template shown below, draw examples of (a) an asymmetrically oriented integral membrane protein, (b) a transmembrane protein, (c) a peripheral membrane protein and (d) a lipid-linked membrane protein.



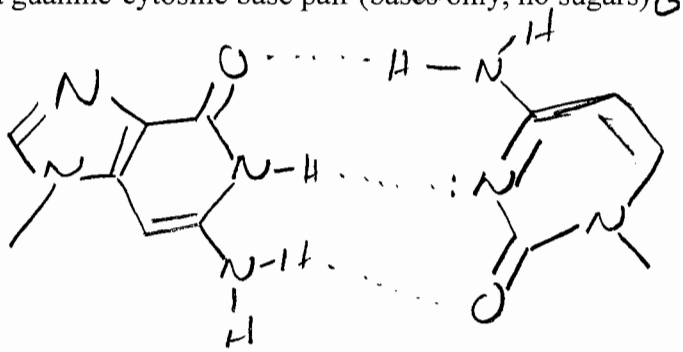
 Name _____

(7) (15 points) In the spaces provided, draw the structures of the indicated molecules

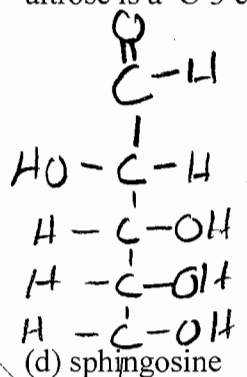
(a) 1-stearoyl-2-oleoyl-3-phosphatidylcholine

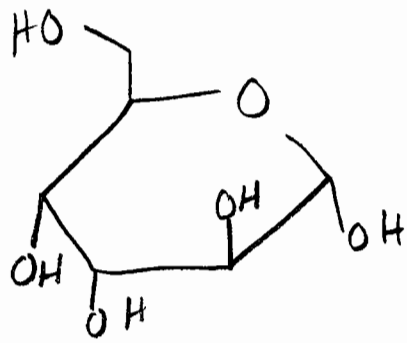


(b) a guanine-cytosine base pair (bases only, no sugars) Guanine, C on right

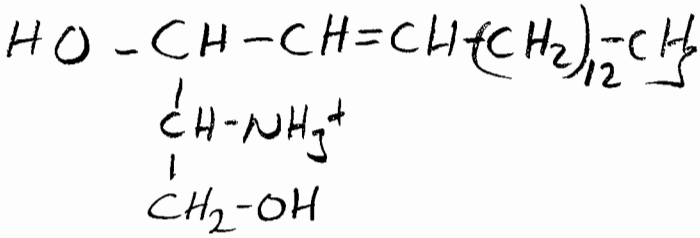


(c) D-altrose and alpha-D-altropyranose (draw BOTH the linear and cyclic forms), given that D-altrose is a C-3 epimer of D-mannose, and D-Mannose is a C-2 epimer of D-glucose

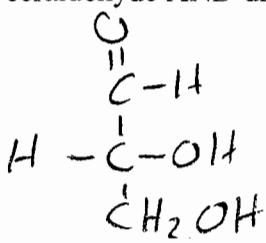


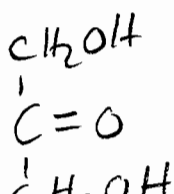


(d) sphingosine



(e) glyceraldehyde AND dihydroxyacetone





 Name _____

(8) Definitions. 20 points.

Name the unbranched form of starch	α- amylose
When relatively high concentrations of ~~triacylglycerols~~ fatty acids are placed in water they form structures known as _____.	micelles
How many stereoisomers are possible for the family of D-ketoses with seven carbon atoms?	$2^{7-3}/2 = 8$
What is the repeating sugar unit and linkage in chitin?	B(1,4)-NAG (N-acetylglucos am
Which hexopyranose sugar contains all bulky groups in equatorial positions?	B-D-glucopyranose (B-D-glc
The compound resulting from the nucleophilic addition of an alcohol to an aldehyde is called what?	hemiacetal
What type of bond joins two sugar units in a disaccharide?	O-glycosidic; O-ether
What type of bond joins a nitrogenous base and sugar?	N-glycosidic; N-ether
What type of membrane protein may be solubilized by high salt concentration or change in pH?	peripheral
What is the repeating sugar unit and linkage in peptidoglycan?	B1,4 (NAM-NAG)
Which nitrogenous base is present in DNA but not RNA?	thymine
What is the name of the family of derivatized polysaccharides that associate with proteins in the extracellular matrix of animal cell tissue	glycosaminoglycans
What specific two types of sugar linkages are found in glycogen?	α(1,4)glc + α(1,6)glc
Ring-cyclized sugars that contain a free hydroxyl group at the anomeric carbon are called _____ sugars	reducing
The inhibition of an enzyme by a downstream product of a metabolic pathway is called what?	feedback inhibition
What vitamin is associated with vision?	A
What vitamin is associated with regulating calcium uptake for bone formation?	D
The relations A = T and G =C are called what?	Chargaff's rules
Name a general role for lipids other than serving as an energy reserve or structural component of membranes	hormone, insulation, detergent,
What conformation does double stranded RNA form in solution?	A

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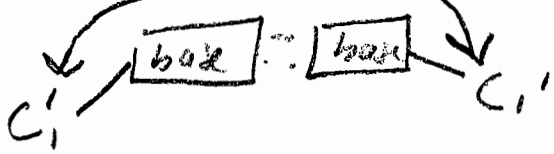
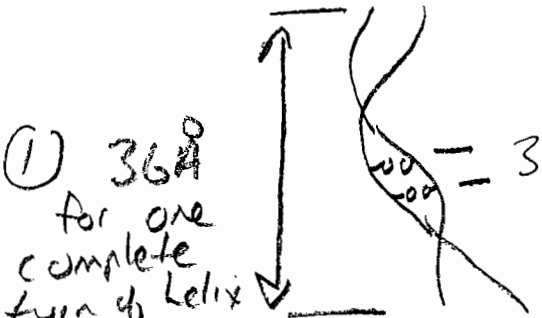
(9) 10 points. Briefly define the following terms as they relate to DNA structure (feel free to use structures/drawings to assist in anwering):

(a) major groove

The side of DNA formed by the larger angle connecting the C_1' carbons of paired bases & the center of the helix axis



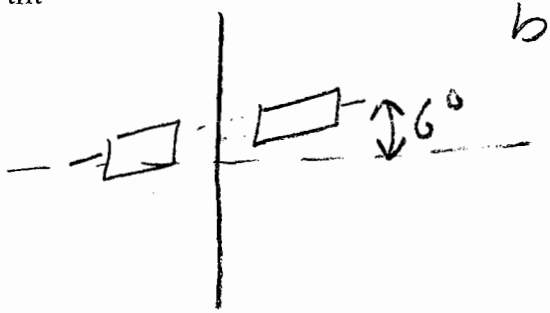
(b) two periodicities



(1) 36Å for one complete turn of helix about its axis

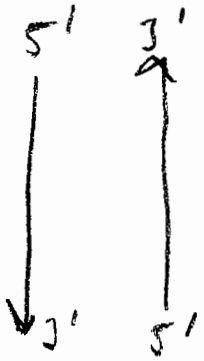
(2) 3.4Å base pair - base pair distance

(c) base tilt



base pairs are tilted slightly (~6°) relative to a line perpendicular to the helix axis

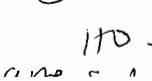
(d) anti parallel



two chains are complementary, not identical & run in different directions

(e) sugar pucker

1 of 4 C atoms of sugar ring in ribose or deoxyribose is out of plane of the remaining atoms



(10) (4 points)
How do the following alterations to a lipid bilayer affect fluidity and the transition temperature and why?

(a) increase degree of fatty acid side chain unsaturation

increase fluidity and decrease trans. temp - unsat'd side chains introduce kinks due to cis conformations so that side chains don't pack as tightly, so less VDW forces

(b) increase length of fatty acid side chains

decrease fluidity and increase trans. temp - longer FA side chains provide more sites for VDW interactions

(11) (4 points) Explain how cholesterol is capable of acting as a membrane plasticizer both in response to higher temperatures and lower temperatures.

higher temperatures - cholesterol acts as a "wedge", preventing unrestricted rotation of FA side chains, helping maintain VDW contacts that maintain bilayer structure

lower temperatures - cholesterol prevents formation of stronger VDW forces by inserting between adjacent phospholipid side chains, helping maintain fluidity