Supramolecular Chemistry

Tentamen 28-10-~~2014~~ 2015

Time: 3 hours

Name :
Student registration number :

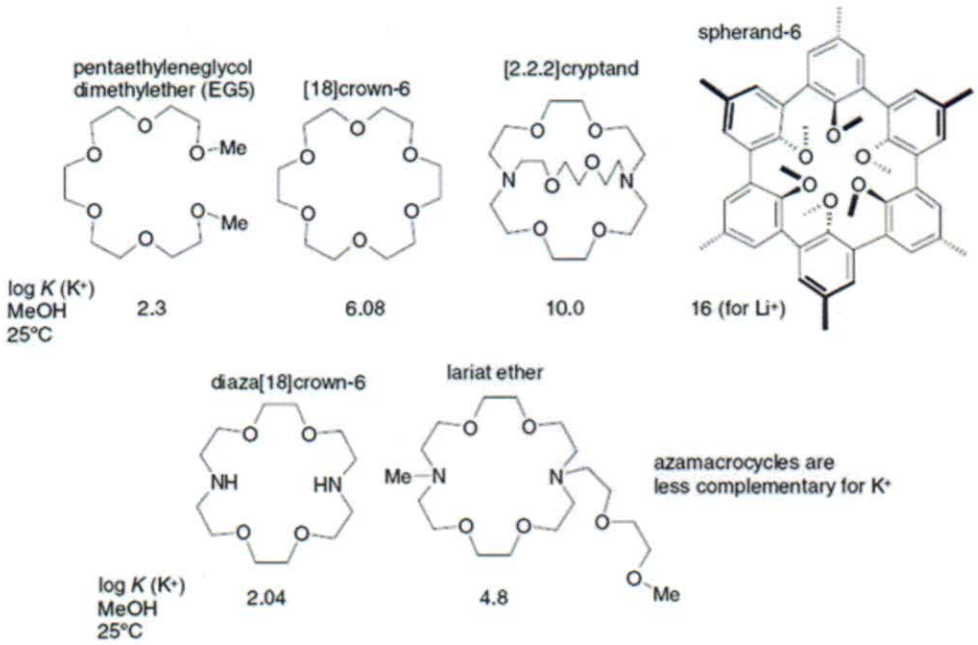
Always explain your answer

SCORE

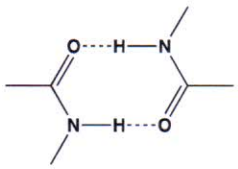
Question	1	2	3	4	5	6	7	8	9		Totaal
Max score	15	10	10	15	10	10	10	10	10		100
Score											

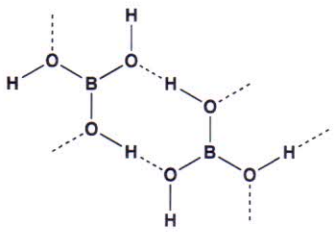
1a What is meant by allosteric binding in a host-guest complex? Give a(n) (schematic) example

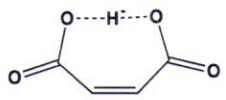
1b Explain the observed trend in the binding of potassium

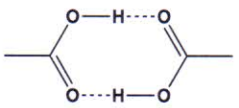


2) Arrange the molecules below in terms of increasing hydrogen bond strength. b) Explain in detail the mechanism(s) by which the hydrogen bond is strengthened for each.

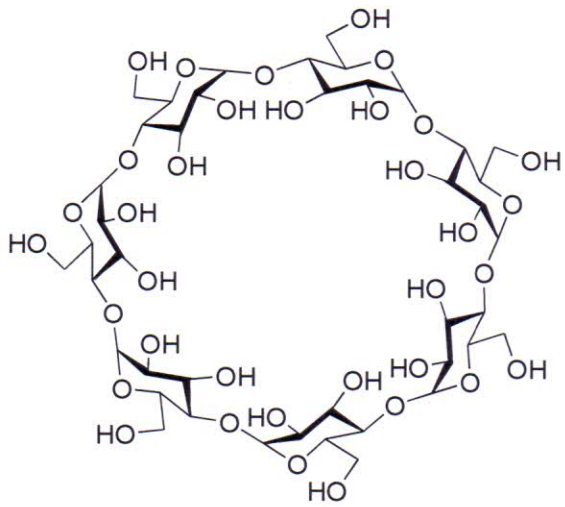








3) Describe the driving forces for binding of toluene in beta-cyclodextrin in an aqueous solution. Explain the binding also in (qualitative) terms of entropy and enthalpy. What do you expect to be the sign of the free energy?

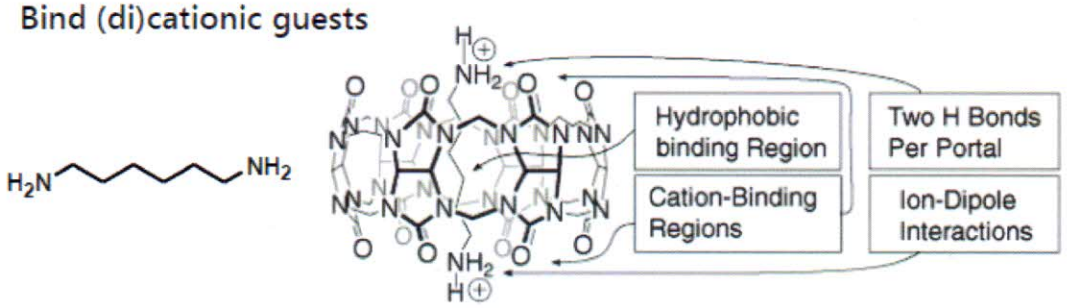


4) Explain the steps involved in preparing a DNA octahedron using structural DNA nanotechnology from concept to final product. i.e. what are the critical steps that need to be taken to ensure correct structure formation? What types of building blocks would you use, and why? b) What are the experimental techniques that you can use to prove its formation? List several indirect and direct methods and explain how this experiment would contribute to unraveling the structure of the octahedron.

5a) Cucurbiturils can catalyze the shown click reaction. Explain why the reaction is regioselective and why product inhibition is observed.

Cucurbiturils

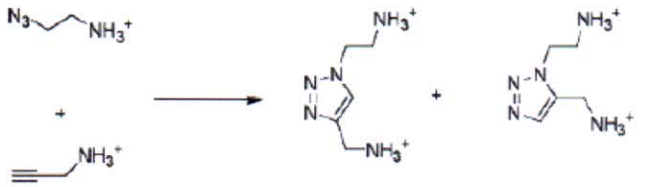
Bind (di)cationic guests



K_a = 2.8 x 10^6 M^{-1}

Applications

- Removal of charged dyes and (heavy) metals from textile waste streams
- Supramolecular reaction chamber for regioselective click reaction



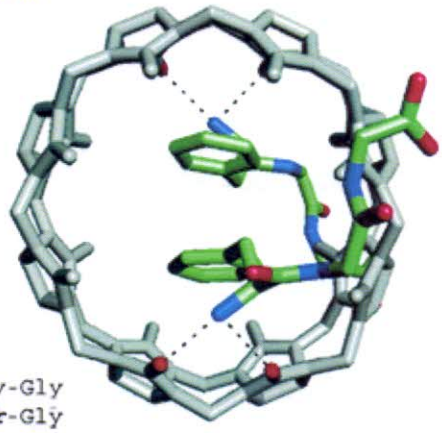
- Only the 1,4-isomer is formed
- Acceleration 55,000x
- Product inhibition, why?

5b) Many synthetic and natural receptors show the highest affinity for a guest when this 55% rule is obeyed. Why is this?

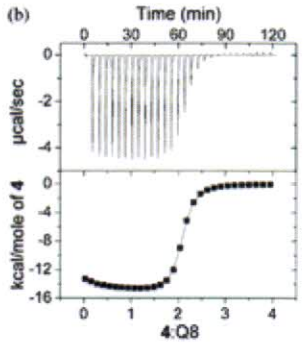
6) List 5 key differences between DNA and RNA. b) Explain how these differences can contribute to the design and synthesis of building blocks for nucleic acid nanotechnology and their subsequent nucleic acid nanostructures.

7a) When looking at the binding of tripeptides **1** and **4** in Cucurbituril, what are the driving forces (i.e. non-covalent interactions) for binding? Explain your answer.

Supramolecular Control of Enzyme Activity through Cucurbit[8]uril-Mediated Dimerization



Cucurbit[8]uril + 2 Phe-Gly-Gly $\underset{H_2O,\ pH\ 7.0}{\overset{K = 10^{11}\ M^{-2}\ cooperative}{\rightleftharpoons}}$



1	***Trp***-Gly-Gly	7	***Tyr***-Gly-Gly
2	Gly-***Trp***-Gly	8	Gly-***Tyr***-Gly
3	Gly-Gly-***Trp***	9	Gly-Gly-***Tyr***
4	***Phe***-Gly-Gly	10	***His***-Gly-Gly
5	Gly-***Phe***-Gly	11	Gly-***His***-Gly
6	Gly-Gly-***Phe***	12	Gly-Gly-***His***

Table 2. Thermodynamic Binding Data for Ternary Complexes of **1** and **4** with Q8

complex	K_{tet}[a] (M^{-2})	ΔG_{tet}[b] (kcal/mol)	ΔH_{tet}[c] (kcal/mol)	$-T\Delta S_{tet}$[d] (kcal/mol)
Q8·**1**$_2$	$(3.6 \pm 0.9) \times 10^9$	−13.1 (±0.2)	−22.8 (±0.5)	9.7 (±0.6)
Q8·**4**$_2$	$(1.5 \pm 0.2) \times 10^{11}$	−15.4 (±0.1)	−29.6 (±0.2)	14.2 (±0.3)

J. Am. Chem. Soc. 2006, 128, 12574-12581.

7b) Why is this system highly selective for tripeptides **1** and **4**. And why does it form a 1:2 complex?