

Sample examination # 2 questions

**Partial periodic table**

Atomic numbers and electronegativities

<i>IA</i>	<i>IIA</i>	<i>IIIA</i>	<i>IVA</i>	<i>VA</i>	<i>VIA</i>	<i>VIIA</i>	<i>VIIIA</i>
1 <b>H</b> 2.20							2 <b>He</b> —
3 <b>Li</b> 0.98	4 <b>Be</b> 1.57	5 <b>B</b> 2.04	6 <b>C</b> 2.55	7 <b>N</b> 3.04	8 <b>O</b> 3.44	9 <b>F</b> 3.98	10 <b>Ne</b> —
11 <b>Na</b> 0.93	12 <b>Mg</b> 1.31	13 <b>Al</b> 1.61	14 <b>Si</b> 1.90	15 <b>P</b> 2.19	16 <b>S</b> 2.58	17 <b>Cl</b> 3.16	18 <b>Ar</b> —
19 <b>K</b> 0.82	20 <b>Ca</b> 1.00	31 <b>Ga</b> 1.81	32 <b>Ge</b> 2.01	33 <b>As</b> 2.18	34 <b>Se</b> 2.55	35 <b>Br</b> 2.96	36 <b>Kr</b> —
37 <b>Rb</b> 0.82	38 <b>Sr</b> 0.95	49 <b>In</b> 1.78	50 <b>Sn</b> 1.88	51 <b>Sb</b> 2.05	52 <b>Te</b> 2.10	53 <b>I</b> 2.66	54 <b>Xe</b> —
55 <b>Cs</b> 0.79	56 <b>Ba</b> 0.89	81 <b>Tl</b> 1.83	82 <b>Pb</b> 2.10	83 <b>Bi</b> 2.02	84 <b>Po</b> 2.00	85 <b>At</b> 2.20	86 <b>Rn</b> —

**Interaction*****E*strain  
[kJ/mol]**

CH <sub>3</sub> ,H 1,3-diaxial	3.6
CH <sub>3</sub> ,CH <sub>3</sub> <i>gauche</i>	3.8
H,H eclipse	4.0
CH <sub>3</sub> ,H eclipse	6.0
CH <sub>3</sub> ,CH <sub>3</sub> eclipse	11

**Eyring equation**

$$k = (k_B T/h) e^{-\Delta E^\ddagger/RT}$$

$$k = (6.21 \times 10^{12}) e^{-0.404 E^\ddagger} \text{ s}^{-1} \text{ (at 25 }^\circ\text{C)}$$

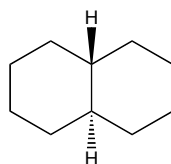
**Equilibrium constant**

$$K_{eq} = e^{-\Delta G^\circ/RT}$$

$$K_{eq} = e^{-0.404 \Delta G^\circ} \text{ (at 25 }^\circ\text{C)}$$

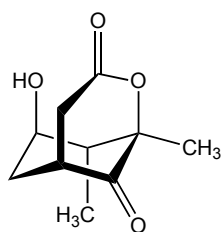
**Standard enthalpies of formation  $\Delta H_f^\circ$** 

-123 kJ/mol

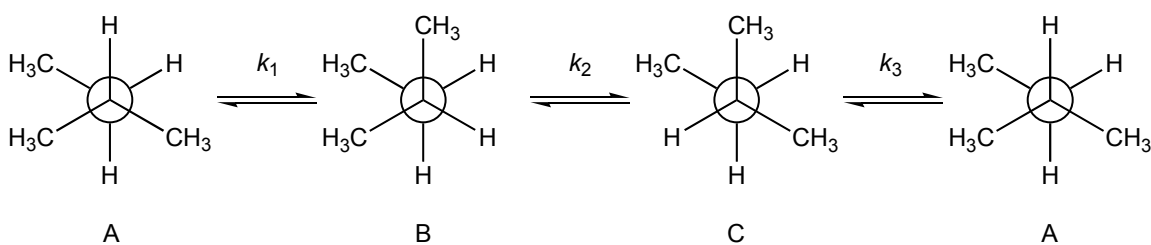


-182 kJ/mol

**(1)** Determine the absolute configuration (*R* or *S*) of all the  $sp^3$ -hybridized chirality centers in this molecule.



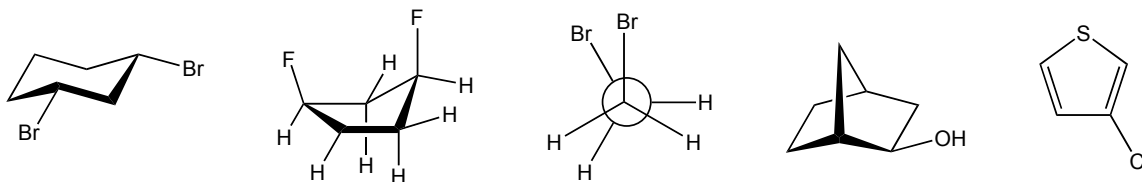
**(2)** Consider the  $360^\circ$ -rotation of the C2–C3 bond of 2-methylbutane shown below:



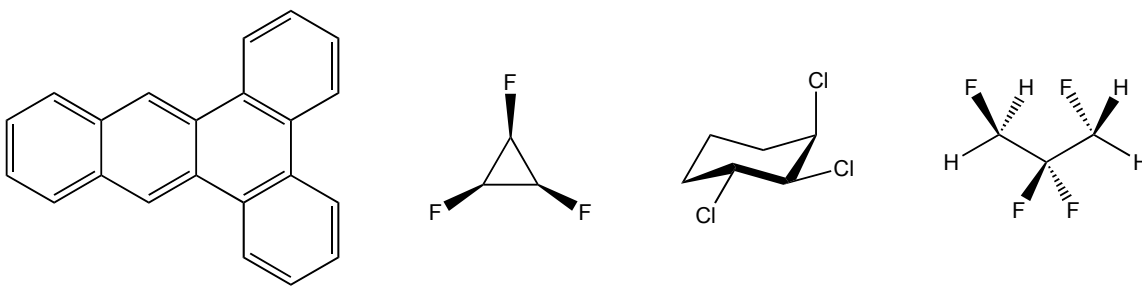
**(a)** Calculate to two significant figures the rate constants  $k_1$ ,  $k_2$ , and  $k_3$  at  $25^\circ\text{C}$  of each conformational change.

**(b)** Calculate to two significant figures the percentages of conformations A, B and C at equilibrium at  $25^\circ\text{C}$ .

**(3)** Circle the structures that are chiral.



**(4)** Indicate the number and kind of each symmetry element, if any, in these molecules.

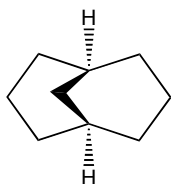


**(5a)** Draw the two interconverting chair conformations of (1*S*,2*S*,4*R*)-1,2,4-trimethylcyclohexane.

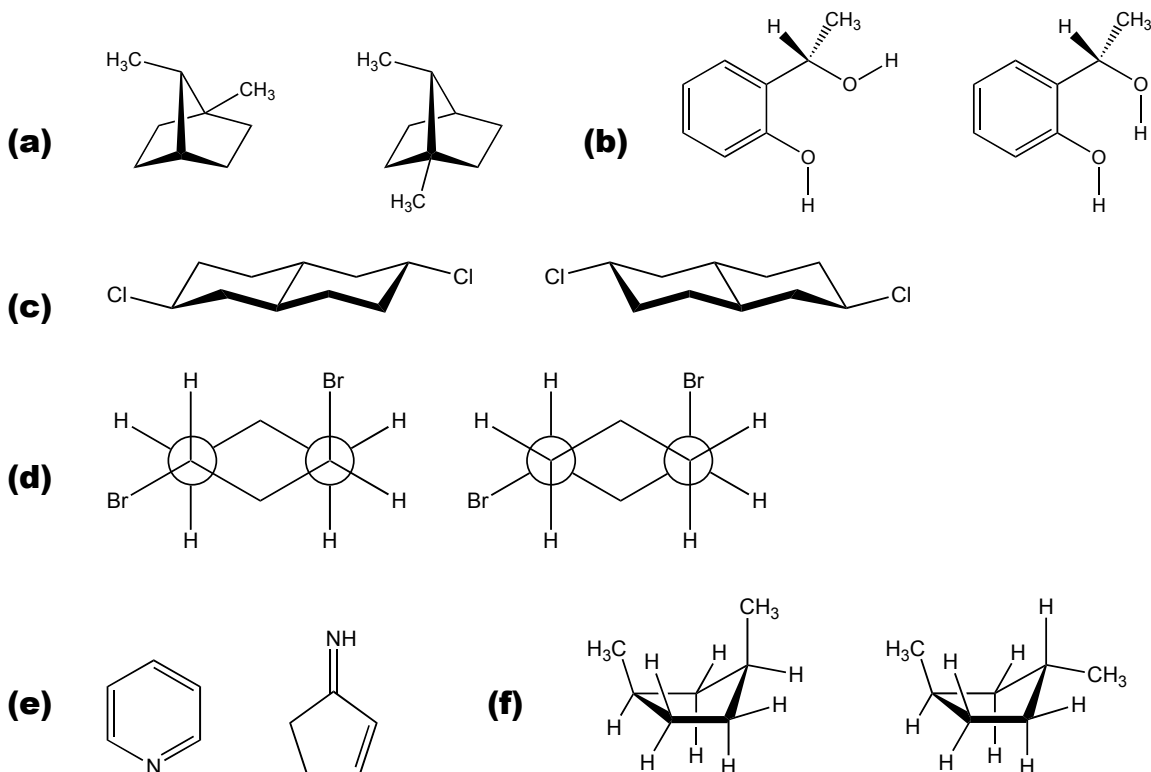
**(5b)** Calculate the strain energy  $E_{strain}$  of both chair conformations.

**(5c)** Calculate to two significant figures the percentages of each chair conformation at equilibrium at 25 °C.

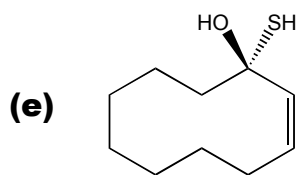
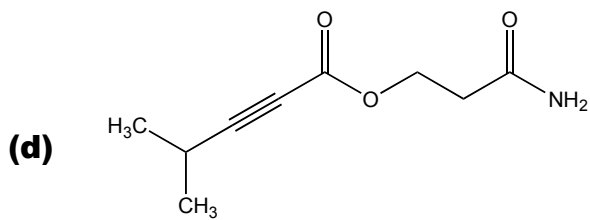
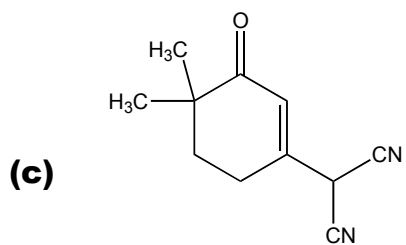
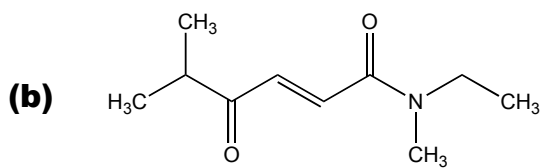
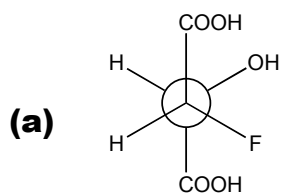
**(6)** Calculate the strain energy  $E_{strain}$  of this molecule given that its standard enthalpy of formation  $\Delta H^{\circ}f = -128$  kJ/mol.



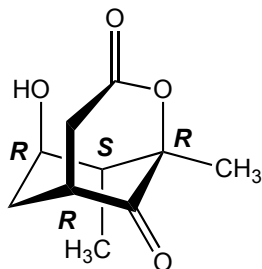
**(7)** Indicate whether each pair of structures represent (1) enantiomers, (2) diastereomers, (3) constitutional isomers, (4) identical structures, or (5) neither enantiomers, diastereomers, constitutional isomers nor identical structures.



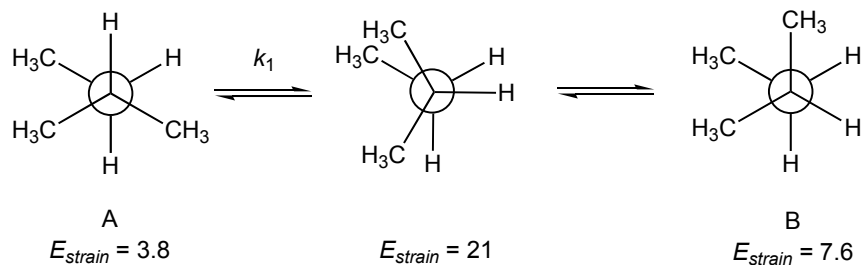
**(8)** Write the systematic name of these compounds.



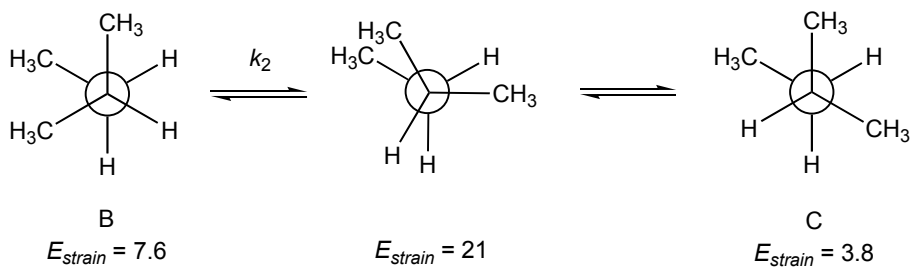
**Answers**  
**(1)**



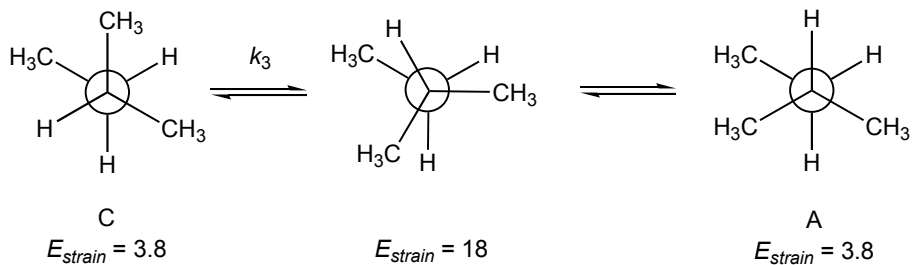
**(2a)**



$$k_1 = (6.21 \times 10^{12})e^{-0.404(21 - 3.8)} \text{ s}^{-1} = 6.0 \times 10^9 \text{ s}^{-1}$$



$$k_2 = (6.21 \times 10^{12})e^{-0.404(21 - 7.6)} \text{ s}^{-1} = 2.8 \times 10^{10} \text{ s}^{-1}$$



$$k_3 = (6.21 \times 10^{12})e^{-0.404(18 - 3.8)} \text{ s}^{-1} = 2.0 \times 10^{10} \text{ s}^{-1}$$

**(2b)**

$K_{eq} = [B]/[A] = e^{-0.404(7.6 - 3.8)} = 0.22$ , that is, for every 0.22 molecule of B, there is 1 molecule of A.

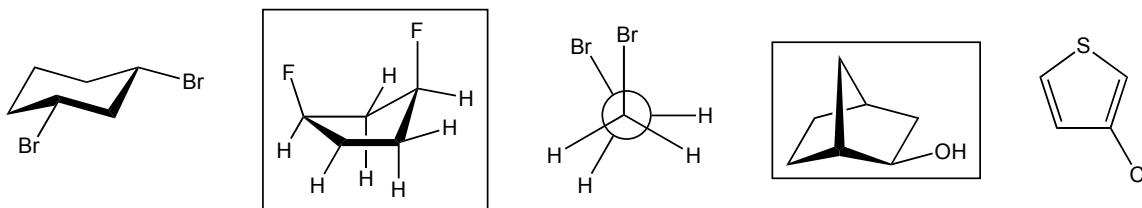
$K_{eq} = [C]/[A] = e^{-0.404(3.8 - 3.8)} = 1$ , that is, for every 1 molecule of C, there is 1 molecule of A.

$$\%A = 100\% \times 1/(1 + 0.22 + 1) = 45\%$$

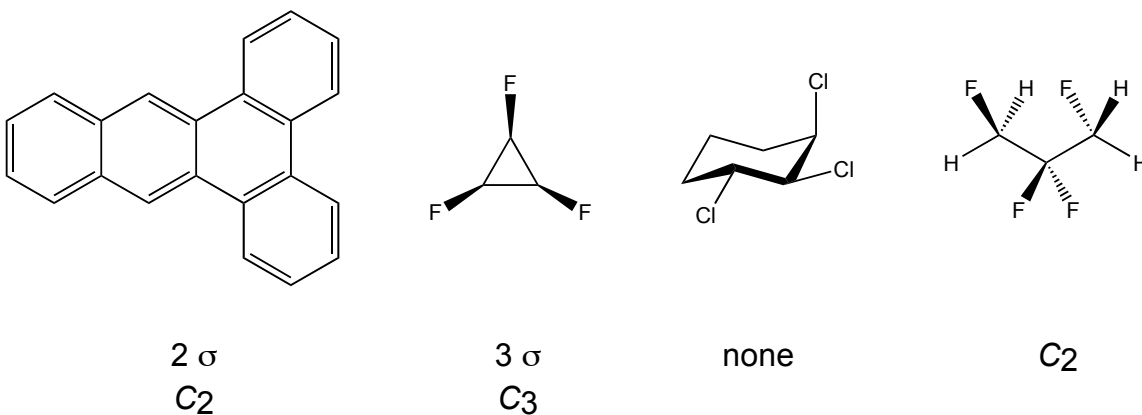
$$\%B = 100\% \times 0.22/(1 + 0.22 + 1) = 10\%$$

$$\%C = 100\% \times 1/(1 + 0.22 + 1) = 45\%$$

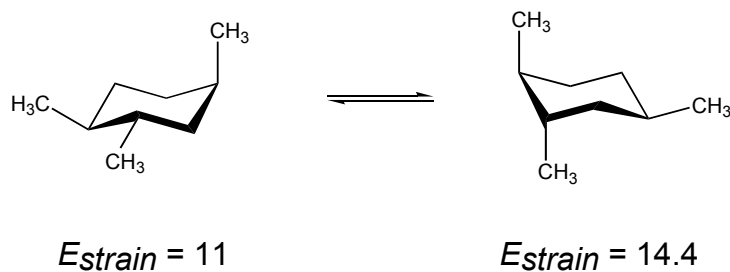
**(3)**



**(4)**



(5)

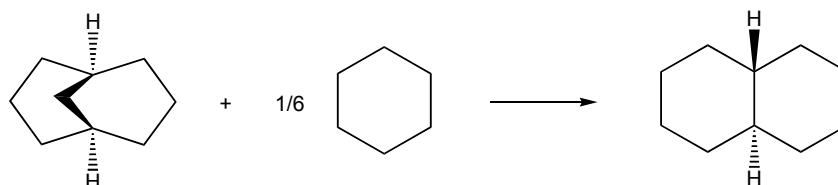


$K_{\text{eq}} = [\text{product chair}]/[\text{reactant chair}] = e^{-0.404(14.4 - 11)} = 0.25$ , that is, for every 0.25 molecule of the product chair, there is 1 molecule of the reactant chair.

% product =  $100\% \times 0.25/(1 + 0.25) = 20\%$

% reactant =  $100\% \times 1/(1 + 0.25) = 80\%$

(6) The homodesmotic reaction is



$$\Delta H^{\circ}_{\text{rxn}} = (-182) - (-128) - (1/6)(-123) = -33.5 \text{ kJ/mol}$$

$$E_{\text{strain}} = 33.5 \text{ kJ/mol}$$

(7a) enantiomers (7b) diastereomers (7c) identical (7d) enantiomers

(7e) neither enantiomers, diastereomers, constitutional isomers nor identical

(7d) diastereomers

(8a) (2R,3S)-2-fluoro-3-hydroxybutanedioic acid (8b) N-ethyl-5,N-dimethyl-4-oxo-2-hexen-1-amide (8c) 2-(4,4-dimethyl-3-oxo-1-cyclohexenyl)-1,3-propanedinitrile (8d) 2-aminocarbonylethyl 4-methyl-2-pentyn-1-oate (8e) (1S)-1-mercapto-2-cyclodecen-1-ol