CNM 7292 (Fall '04)

Key: Exam 2 (take-home part)

1. This compound has a low barrier to rotation about the C=C bond due to a large contribution of the resonance structure on the far right:

\[
\begin{align*}
\text{H-C} = \text{C-} & \text{H} \\
\text{N} & \text{N(CH}_3\text{)}_2 \\
\text{H-C} = \text{C-} & \text{H} \\
\text{N} & \text{N(CH}_3\text{)}_2
\end{align*}
\]

2. (9) b) They are diastereomers.
(a) Vioxx® has the following structure:

(b) In this form Vioxx® does not have any chirality centers.

Cis-decalin has 3 more gauche-butane interactions than trans-decalin. Those three are indicated in the cis form as follows:
(5) I believe the hydroxymethyl group that has been oxidized is pro-S (this is tricky to assign and the usual way where the same atom/group is bonded to the same proximal center does not apply!)

(6) If major enant = $x$ and minor enant = $y$, then

$$x + y = 100 \quad \text{and} \quad x - y = 97$$

Solving the 2-epoch and 2-variables gives:

$$x \text{ (major enant)} = 98.5\% \quad \text{and} \quad y \text{ (minor enant)} = 1.5\%$$

(6) (a) Half-chair conformer of cyclohexane is $C_2$ symmetry

(b) Twist-bend conformer is $D_2$ symmetry.

(7) The sketch of the next page uses the graph from Figures 3.1 and 3.5 to assume the following: $GB \sim 0.8$ kcal/mol; an eclipsing CH$_2$-CH$_3$ is $\sim 2.7$; an eclipsing H-H is $\sim 1$ kcal/mol; an eclipsing CH$_3$-H $\sim 1.2$ kcal/mol.  

(5)
(a) In the exam you took, the interaction between axial Me groups was written as 2.8 kcal/mol, instead should have been ~ 3.7 kcal/mol. Using this value gives:

\[ 3 \text{ Me-Me} \times 3.7 = 11.1 \text{ kcal/mol} \]

(b) \( \Delta G = -RT \ln K \)

\( \text{substituting} \ 11,100 \text{ kcal/mol} \) for \( \Delta G \): 

(b) Let's do this problem as follows:

\( \Delta G = -11.1 \text{ kcal/mol} \)

Use \( \Delta G = -RT \ln K \) where \( R = 1.987 \text{ cal/K mol} \) and \( T = 298 \text{ K} \) gives the following:
\[-11,100 \text{ cal} \left( \frac{1 \text{ cal}}{1 \text{ J}} \right) \left( \frac{258 \text{ K}}{2} \right) \ln K = -1.987 \text{ cal} \left( \frac{1 \text{ cal}}{1 \text{ J}} \right) \ln K \]

\[\Rightarrow \ln K = -18.7\]

so \[K = 1.3 \times 10^8\]

This essentially means there is hardly any of the "all-\(\text{ax}\)" conformer present! It is way greater than \(99.999\%\)!