Interactive Energies, kcal/mol

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Gauche</th>
<th>Eclipsing</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/H</td>
<td>~1.0</td>
<td>~1.4</td>
</tr>
<tr>
<td>Me/Me</td>
<td>~2.6</td>
<td>~0.95</td>
</tr>
<tr>
<td>Et/Me</td>
<td>~0.95</td>
<td>~2.8</td>
</tr>
<tr>
<td>i-Pr/Me</td>
<td>~1.1</td>
<td>~2.7</td>
</tr>
<tr>
<td>t-Bu/Me</td>
<td>~2.7</td>
<td>~3.1</td>
</tr>
</tbody>
</table>

Infrared Correlation Chart

- O-H: 3000–3100 cm⁻¹, broad
- C=O: 1700–1750 cm⁻¹, strong
- C≡N: 2200–2300 cm⁻¹, broad
- N-H: 3000–3600 cm⁻¹, broad

NMR Correlation Charts

- R-NH₂: variable and condition dependent, ca. 2 - 6 ppm
- R-OH: 3.5 ppm
- Aromatic: 7.0 – 8.5 ppm

Answer Key

(Answer to specific questions provided on the page.)
YOU MUST COMPLETE THIS PAGE WITH YOUR NAME
(EVEN THOUGH YOU ALREADY DID THIS ON THE COVER PAGE)
AND ALSO GIVE YOUR ASU OR POSTING ID NUMBER
WE NEED THIS NUMBER BECAUSE YOU WOULDN'T BELIEVE THE NUMBER OF
STUDENTS WHOSE NAMES WE CAN'T READ!

Points by question

1 ____________/14
2 ____________/26
3 ____________/26
4 ____________/24
5 ____________/27
6 ____________/34
7 ____________/24

Points Removed for cover errors ____/2

Extra Credit ____/5

Total (incl Extra) ________/175+5

"YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM"
Question 1 (14 pts) Give the IUPAC name for the following structure

4-cyclopentyl-3-ethyl-2,8-dimethylnonane

Question 2 (26 pts.)

a) Draw both chair conformations for the provided cyclohexane and calculate the energy difference between the chairs. Indicate CLEARLY which energy factors you are taking into account for each chair. **INDICATE WHICH IS THE LOWEST ENERGY CHAIR**

b) Each carbon in the provided cyclohexane is labelled a, b, c, d etc. Label the carbon atoms on your chairs with the letters a, b, c etc. to identify exactly which carbons in your chairs correspond to which carbons in the provided structure

EXTRA CREDIT (5 pts) Which types of structures are the primary constituent of gasoline?

alkenes  ketones  **alkanes**  aromatics
Question 3 (26 pts.) For 3,3-dimethylhexane:

a) Draw a line-angle structure.

b) For rotation around the C3-C4 bond, draw Newman projections AND 3D (sawhorse) structures for BOTH the HIGHEST and the LOWEST energy conformations, (clearly indicate which is which). Your Newman projections should look FROM carbon 3 TO carbon 4.

![Newman projections and 3D structures for 3,3-dimethylhexane](image)

c) Determine the energy difference between these two conformations. CLEARLY indicate the energy factors that you included in your calculation of this energy difference.

\[
\begin{align*}
\text{lowest E conformation:} & \quad 2 \text{ Et/Me gauche} = 2 \times 0.95 = 1.9 \\
& \quad \text{Total} = 1.9 \text{ kcal/mol} \\
\text{highest E conformation:} & \quad 2 \text{ Me/H eclipse} = 2 \times 1.4 = 2.8 \\
+ & \quad 1 \text{ Et/Et eclipse} = 3.1 \\
& \quad \text{Total} = 5.9 \text{ kcal/mol} \\
\end{align*}
\]

\[\Delta E = 5.9 - 1.9 = 4.0 \text{ kcal/mol}\]

Question 4 (24 pts.) The vibration frequencies for the two C=O bonds in A and B are different. Which would have the higher vibration frequency? Give a brief explanation in terms of minor resonance contributors as appropriate. Include drawings of any relevant minor resonance contributors, with all curved arrow pushing, resonance brackets and arrows.

![Resonance contributors for C=O bonds](image)

structure A has a minor resonance contributor that has a single C-O bond, AND it contributes more to the resonance mixture than the other minor contributors because it has two formal pi-bonds.

structure A has more single bond character in the C=O bond, the C=O bond is thus weaker and vibrates with a lower frequency.
Question 5 (27 pts.) Assign the provided IR spectra to ONE of the FOUR provided structures A - D (two of the structures do not have a provided spectrum). On each spectrum, **identify the peaks that are associated with a specific functional group or type of C-H bond by drawing the functional group or bond and drawing an arrow from the specific bond in the functional group that vibrates to the absorption peak.**

```
A
\begin{align*}
\text{sp2} & \quad \text{sp3} \\
\text{H} & \quad \text{C}
\end{align*}
```

```
B
\begin{align*}
\text{sp2} & \quad \text{sp3} \\
\text{H} & \quad \text{C}
\end{align*}
```

```
C
\begin{align*}
\text{sp2} & \quad \text{sp3} \\
\text{H} & \quad \text{C}
\end{align*}
```

```
D
\begin{align*}
\text{sp2} & \quad \text{sp3} \\
\text{H} & \quad \text{C}
\end{align*}
```

```
\begin{align*}
\text{3346} & \quad 3004 \\
3009 & \quad 2901 \\
1692 & \quad 1470 \\
1386 & \quad 1279 \\
1171 & \quad 975
\end{align*}
```

```
\begin{align*}
\text{3389} & \quad 2963 \\
2935 & \quad 2876 \\
2820 & \quad 2725 \\
1708 & \quad 1467 \\
1386 & \quad 1036 \\
947 & \quad 1134
\end{align*}
```

this spectrum corresponds to structure A

this spectrum corresponds to structure D
Question 6 (34 pts.)

a) Explain which of the bonds C-Ha or C-Hb has the larger homolytic bond dissociation energy. Give an explanation that includes drawings of the products of EACH bond dissociation, including all relevant resonance contributors as appropriate. Include the curved arrow pushing showing how the electron distributions "move" between each contributor and resonance arrows/brackets.

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the Ha-C bond has the smaller bond dissociation energy since the radical formed is stabilized by 3 resonance contributors compared to 2 for dissociation of the Hb-C bond
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b) Draw an ENERGY DIAGRAM with properly labelled axes for cleavage of the C-Ha and C-Hb bonds ON THE SAME DIAGRAM, clearly indicating which diagram refers to which bond cleavage and indicate the MAGNITUDES of the two bond dissociation energies on your diagrams. Deciding where to normalize the diagrams is part of the problem so please don't ask for help with that part.
Question 7 (24 pts.) For the following structure:

a) Draw all reasonable resonance contributors, show how they are related using the curved arrow-pushing formalism. Do not forget formal charges and non-bonding electrons as appropriate and resonance arrows and brackets.

b) Indicate which is the **MAJOR** and which is the **MINOR** resonance contributor and give a BRIEF explanation for your choices. If there are equal major or minor indicate so.

c) Draw the "actual" resonance hybrid structure using the delta notation to indicate partial charges.

d) On your actual structure, indicate which atom will have the LARGEST partial negative charge.

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the major resonance structure has the formal charge on the most electronegative atom
the minor resonance structure has the formal charge on the least electronegative atom

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make sure you answer all FOUR parts of this problem!