1. (29 pts. total.) Consider the acetonitrilium ion, [CH$_3$CNH]$^+$. 

(a) (4 pts.) How many valence electrons does [CH$_3$CNH]$^+$ have? (Note the charge!)

\[(2 \times 4) + (4 \times 1) + 5 - 1 = 16\] valence electrons

(b) (5 pts.) Using the $\sigma$ bond network drawn below as a starting point, draw the BEST resonance structure for the acetonitrilium ion. Be sure to show all lone pairs.

\[ 
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{C} \\
\text{C} \equiv \text{N} \\
\text{H} \\
\text{H} \\
\end{array} 
\]

(c) (6 pts.) Looking at the structure you just drew, what are the hybridizations of:

- the left-hand C? \(\text{sp}^3\)
- the right-hand C? \(\text{sp}\)
- the N? \(\text{sp}\)

(d) (4 pts.) Considering your answer to (c), what is the C–C–N bond angle in the acetonitrilium ion?

\[180^\circ\]
(e) (10 pts.) Draw a diagram showing all of the atomic orbitals in the acetonitrilium ion. Indicate which atomic orbitals overlap to form $\sigma$ bonds, which ones overlap to form $\pi$ bonds, and which ones hold unshared electrons. I’ve drawn out the C–H bonds to get you started. (Note: For sake of clarity, please don’t draw the small back lobes of the hybrid orbitals.)
2. (5 pts. each, 15 pts. total.) The best resonance structure of each of the following compounds is shown. Draw the second best resonance structure (or an equally good resonance structure) of each one.

(a)

\[\begin{align*}
\text{H} & \quad \text{H}\quad \text{NH}_2 \\
\text{H} & \quad \text{H}\quad \text{NH}_2
\end{align*}\]

(b)

\[\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C}_5\text{H}_5\text{H} & \quad \text{H} \\
\text{C}_5\text{H}_5\text{H} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}\]

(c)

\[\begin{align*}
\text{H} & \quad \text{H}\quad \text{H}\quad \text{H} \\
\text{H} & \quad \text{H}\quad \text{H}\quad \text{H} \\
\text{H} & \quad \text{H}\quad \text{H}\quad \text{H} \\
\text{H} & \quad \text{H}\quad \text{H}\quad \text{H}
\end{align*}\]

or others
3. (9 pts. total) The structures of uridine (an RNA base), thymidine (a DNA base), and AZT (an anti-AIDS drug), are shown.

(a) (4 pts.) How many hydrogen atoms does uridine have?
12

Use words, not numbers, to answer part (b).

(b) (5 pts.) What is the oxidation state:

- of C1 in uridine? _aldehyde_
- of C2 in uridine? _alcohol_
- of C2 in thymidine? _alkane_
- of C3 in thymidine? _alcohol_
- of C3 in AZT? _alcohol_
(4) (12 pts. total.)

(a) How many degrees of unsaturation does C₅H₇ClO have? (4 pts.)

2

(b) Draw an isomer of C₅H₇ClO that contains a ketone (C=O-C). (There are many correct answers.) (4 pts.)

(c) Draw an isomer of C₅H₇ClO that does not contain a ketone. (Again, there are many correct answers.) (4 pts.)
(5) (5 pts. each, 25 pts. total.) For each pair of compounds, indicate the relationship of the second compound to the first by circling the best answer.

(a) 

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{is a skeletal isomer of} \\
\text{is a resonance structure of} \\
\text{is the same compound as (not a resonance structure of)} \\
\text{is not an isomer, but has the same functional group as} \\
\text{has none of the above relationships to}
\end{align*}
\]

(b) 

\[
\begin{align*}
\text{OH} & \quad \text{is a skeletal isomer of} \\
\text{is a resonance structure of} \\
\text{is the same compound as (not a resonance structure of)} \\
\text{is not an isomer, but has the same functional group as} \\
\text{has none of the above relationships to}
\end{align*}
\]

(c) 

\[
\begin{align*}
\text{HN} & \quad \text{is a skeletal isomer of} \\
\text{is a resonance structure of} \\
\text{is the same compound as (not a resonance structure of)} \\
\text{is not an isomer, but has the same functional group as} \\
\text{has none of the above relationships to}
\end{align*}
\]
(d) \[
\begin{align*}
\text{(a)} & \quad \text{is a skeletal isomer of} \\
\text{(b)} & \quad \text{is a resonance structure of} \\
\text{(c)} & \quad \text{is the same compound as (not a resonance structure of)} \\
\text{(d)} & \quad \text{is not an isomer, but has the same functional group as} \\
\text{(e)} & \quad \text{has none of the above relationships to}
\end{align*}
\]

(e) \[
\begin{align*}
\text{(a)} & \quad \text{is a skeletal isomer of} \\
\text{(b)} & \quad \text{is a resonance structure of} \\
\text{(c)} & \quad \text{is the same compound as (not a resonance structure of)} \\
\text{(d)} & \quad \text{is not an isomer, but has the same functional group as} \\
\text{(e)} & \quad \text{has none of the above relationships to}
\end{align*}
\]
6. (5 points each, 10 points total.) Amides are usually much lower in energy than the corresponding ketones because a low-energy resonance structure (B) can be drawn for an amide that cannot be drawn for the ketone:

![Resonance structures](image)

However, the tricyclic amide 1 is *higher* in energy than the corresponding ketone 2, partly because resonance structure B cannot be drawn for amide 1.

![Amide and Ketone Structures](image)

(a) There are two different (but related) reasons why resonance structure B can’t be drawn for amide 1. Give one. (Think about the geometry of the atoms and the orientation of the orbitals in space.)

1. Resonance structure B requires an sp²-hybridized N, which means that all the atoms attached to N must be coplanar with N. This can’t be achieved in 1.

2. Resonance between the N and the C=O requires overlap between a p orbital on N and a p orbital on C. The p orbital on C goes in and out of the page of the paper; the N can’t put a p orbital in this orientation without severely distorting the skeleton of 1.

(b) The disallowance of resonance structure B for amide 1 should make amide 1 *equal* in energy to ketone 2, but in fact it is *higher* in energy. What other factor makes amide 1 higher in energy than ketone 2? Hint: Compare the *second-best* resonance structures in amide 1 and ketone 2.

The second-best resonance structures for 1 and 2 have C⁺–O⁻. This structure is destabilized by the N in 1, which is more electronegative than the C in 2. Normally resonance structure B more than compensates for the destabilizing inductive effect of N in amides, but resonance structure B is not available in 1, so the inductive effect takes over.