Statistics: High score, average, and low score will be posted on the course web site after exam grading is complete. The exam is ready to be picked up when these numbers are posted.

Some questions have more than one answer, even though only one answer may be listed here.

To see the final course grade cutoffs, consult the grading scale on the Chemistry 14C course web page.

1. Contributor A and Contributor B

2. Between thymine resonance contributor A and thymine resonance contributor B, the most significant contributor in structure A. *Thymine resonance contributor A is the only resonance contributor that does not violate any of the resonance contributor preference rules.*

3. Several other equally significant contributors are possible.

4. Guanine has eleven conjugated atoms. *Nine atoms in the rings, the carbonyl oxygen atom, and the NH₂ nitrogen atom.*

5. Guanine. *Guanine has more extensive conjugation than thymine, so guanine has a smaller HOMO-LUMO gap, and thus absorbs lower energy photons.*

6. The barrier to rotation around bond 1 is higher than the barrier to rotation around bond 2 because bond 1 has partial pi character due to conjugation whereas bond 2 does not.

7. All are aromatic.

8. In addition to planarity, aromaticity provides a molecule with electron delocalization and special stability.

9. There are hundreds of molecules that meet this requirement. For example, methyl phenyl ether (H₃COC₆H₅) is not planar because the methyl group does not lie in the plane of the benzene ring.

10. (-)-Nicotine has zero stereocenters with R configuration and one stereocenter with S configuration.

11. Enantiomer and Diastereomer
12. (f) None of these conclusions are valid. There is no relationship between the biological effects of enantiomers.

13. (a) Cellulose
(b) Glucose
(c) Pyranose What the heck are pyranose and puranose?
(d) β-1,4-glycoside

14. (a) CH₂CH₂OCH₂CH₂OCH₂CH₃ Most energy per mole for evaporation = highest boiling point. Carbon-oxygen bonds are more polar than carbon-nitrogen bonds, and thus provide for stronger dipole-dipole forces.

(b) The other molecules all have stronger dipole-dipole, aromatic stacking, and London forces.

(c) Highest water solubility results from a greater number of hydrogen bond donor and acceptor sites within the molecule.

(d) CH₃CH₂O⁻ Does not have the CF₃ inductive effect or larger atomic radius of sulfur.

15. (a) Only this molecule has a conjugate base that enjoys resonance stabilization from the benzene ring as well as the aldehyde carbonyl.

(b) Lowest pKₐ = most acidic = same answer as question 15(a).

16. CH₃CH₂O⁻ + H⁺→ CH₃CH₂OH + H⁺CH₂OH

17. Kₑq > 1 when weakest acid and base are on the right side of the equilibrium. Kₑq < 1 when the weakest acid and base are on the left.

18. Glycerol tristearate is a triacylglyceride or triacylglycerol.
Cholesterol is a steroid.

Theobromine is not a lipid.

19. Cys and Ala

20. Cys and Ala

21. The heterocyclic base is guanine (a purine).

22. **Mass spectrum:** $m/z = 226$ (M): *Molecular weight composed of lowest mass isotopes.*

   *Even number of nitrogen atoms*

   $m/z = 227$ (M+1): 13.5%/1.107 = 12.4 = C_{12} or C_{13}

   $m/z = 228$ (M+2): 32.8% indicates one Cl atom. S and Br absent.

   **Formula** ($C_{12}$): 226 (M) - 144 ($C_{12}$) - 35 (${}^{35}\text{Cl}$) = 47 amu for oxygen, nitrogen, and hydrogen.
<table>
<thead>
<tr>
<th>Oxygens</th>
<th>Nitrogens</th>
<th>35 - O - N = H</th>
<th>Formula</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>35 - 0 - 0 = 35</td>
<td>C_{13}H_{13}Cl</td>
<td>Violates H-rule</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>35 - 16 - 0 = 19</td>
<td>C_{13}H_{16}ClO</td>
<td>Doesn’t fit $^1$H-NMR integrals</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>35 - 32 - 0 = 3</td>
<td>C_{13}H_{13}ClO$_2$</td>
<td>More than three signals in $^1$H-NMR</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>35 - 0 - 28 = 7</td>
<td>C_{13}H_{13}ClN$_2$</td>
<td>No oxygen for C=O in IR</td>
</tr>
</tbody>
</table>

Formula (C$_{13}$): 226 (M) - 156 (C$_{13}$) - 35 (^{25}Cl) = 35 amu for oxygen, nitrogen, and hydrogen.

**IR:**
- **Zone 1:** Alcohol O–H: Present - strong, broad peak at ~3450 cm$^{-1}$.
- Terminal alkyne ≡C–H: Absent - no C≡C peak ~ 2200 cm$^{-1}$; not enough DBE for C≡C, C=O, and benzene ring.

- **Zone 2:** Aryl/vinyl $sp^2$ C–H: Present - peaks > 3000 cm$^{-1}$.
- Alkyl $sp^3$ C–H: Present - peaks < 3000 cm$^{-1}$.
- Aldehyde C–H: Absent - no peak ~2700 cm$^{-1}$.
- Carboxylic acid O–H: Absent - not enough oxygens in formula.

- **Zone 3:** C≡C and C≡N: Absent - no peak ~2200 cm$^{-1}$; not enough DBE for triple bond, C=O, and benzene ring.

- **Zone 4:** C=O: Present at 1716 cm$^{-1}$, Conjugation possible. Ketone possible. Not ester (not enough oxygens), aldehyde (no ~2700 cm$^{-1}$ peak), carboxylic acid (not enough oxygens), or amide (no nitrogen). $^{13}$C-NMR consistent with ketone.

- **Zone 5:** Benzene ring: Present - peaks ~1600 cm$^{-1}$ and ~1500 cm$^{-1}$.
- Alkene: Absent - not enough DBE for benzene ring, C=O, and C=C.
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**1H-NMR:**

<table>
<thead>
<tr>
<th>Chemical shift</th>
<th>Splitting</th>
<th>Integral</th>
<th># H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.23-7.19 ppm</td>
<td>multiplet</td>
<td>5</td>
<td>5 H</td>
<td>Phenyl group ($C_6H_5$)</td>
</tr>
<tr>
<td>4.62 ppm</td>
<td>singlet</td>
<td>1</td>
<td>1 H</td>
<td>OH or CH</td>
</tr>
<tr>
<td>2.94 ppm</td>
<td>singlet</td>
<td>2</td>
<td>2 H</td>
<td>$CH_2$ or $2 \times CH$</td>
</tr>
<tr>
<td>2.85 ppm</td>
<td>triplet</td>
<td>2</td>
<td>2 H</td>
<td>$CH_2$ in $CH_3CH_2$ / $CH_2$ in $CHCH_2CH$ / $2 \times CH$ in $CHCHCH$</td>
</tr>
<tr>
<td>2.75 ppm</td>
<td>triplet</td>
<td>2</td>
<td>2 H</td>
<td>$CH_2$ in $CH_3CH_2$ / $CH_2$ in $CHCH_2CH$ / $2 \times CH$ in $CHCHCH$</td>
</tr>
<tr>
<td>1.84 ppm</td>
<td>singlet</td>
<td>3</td>
<td>3 H</td>
<td>$CH_3$ or $3 \times CH$</td>
</tr>
</tbody>
</table>

**Totals**: 15 $15 H$ $C_6H_5 + OH + CH_2 + CH_2 + CH_3 = C_{10}H_{15}O$

**13C-NMR**: 201.8 ppm singlet = ketone. 141.3 ppm singlet + 128.6 ppm doublet + 127.7 ppm doublet + 125.9 ppm doublet = phenyl group. Ten $13C$-NMR signals < 12 carbons in formula, so some symmetry present (phenyl group).

**Atom check**: $C_{10}H_{15}ClO_2$ (from mass spectrum) - $C_{10}H_{15}O$ ($1H$-NMR) - C=O (IR) = C + Cl. This carbon is not accounted for by the $1H$-NMR so it must not be attached to any hydrogen atoms. Corresponds to $13C$-NMR singlet at 87.2 ppm.

**DBE check**: Five (calculated for $C_{10}H_{15}ClO_2$) - 4 (Ph) - 1 (C=O) = all DBE used.

**Pieces**: Phenyl ($C_6H_5$) / OH / $CH_2$ / $CH_3$ / $C=O$ (ketone) / C (no H) / Cl

**Assembly**: We start, as always, with the $1H$-NMR splitting patterns, which reveal that the pair of $CH_2$ in $CH_2CH_2$ join together to form one $CH_2CH_2$.

**Diagram**:

![Structure Diagram](image-url)