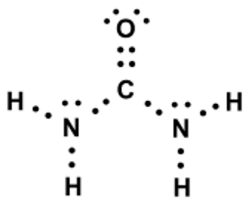
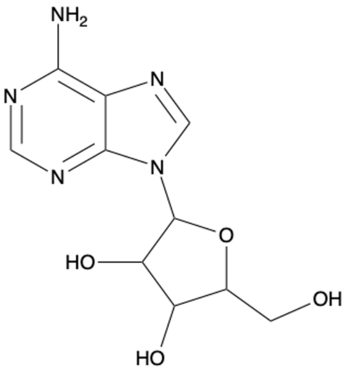
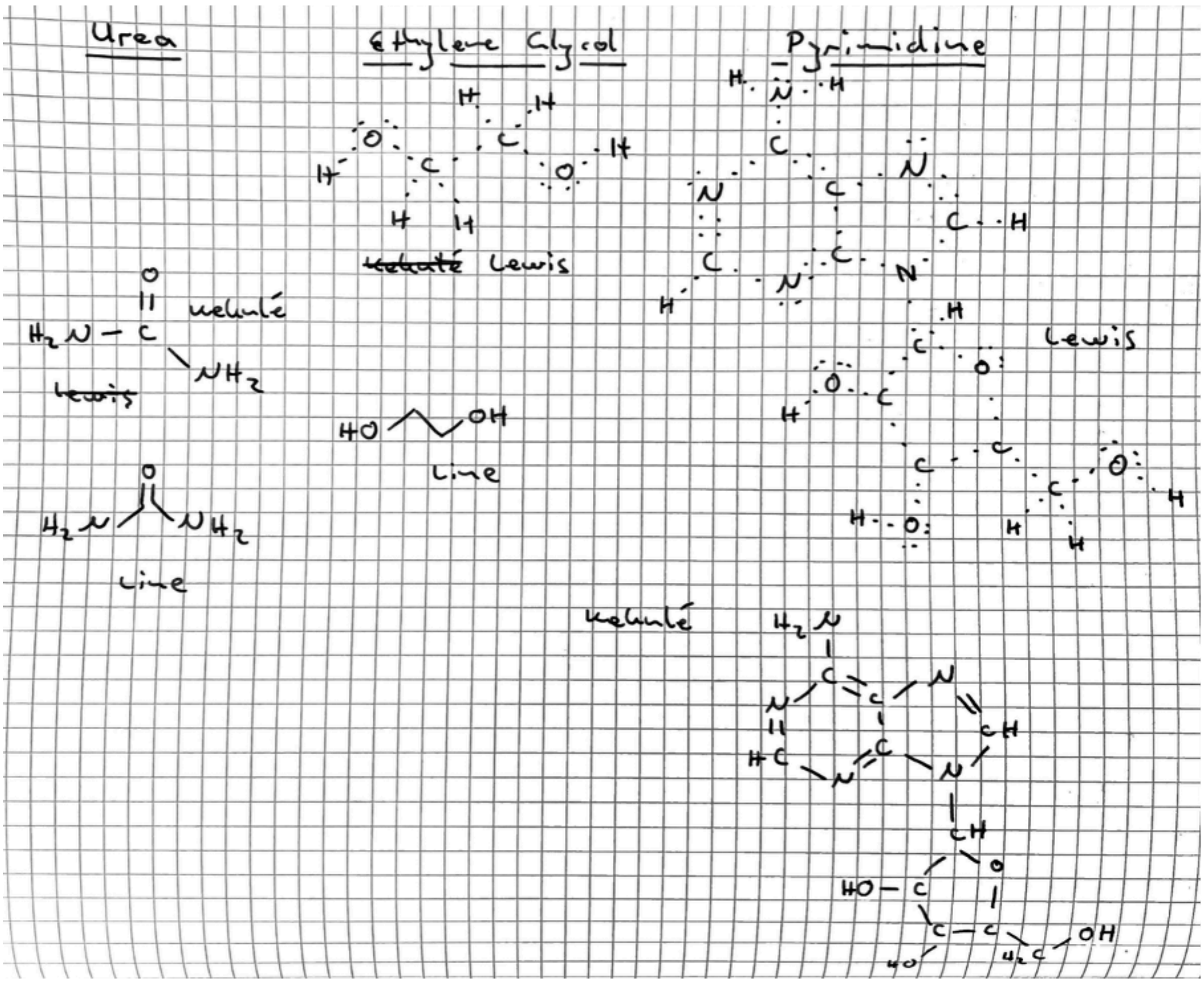
1.1 Drawing Organic Molecules

Organic compounds can be represented in different ways. Complete the examples of urea, ethylene glycol and pyrimidine below with the representations not shown in each case (Kekulé, Lewis, Line Structure).



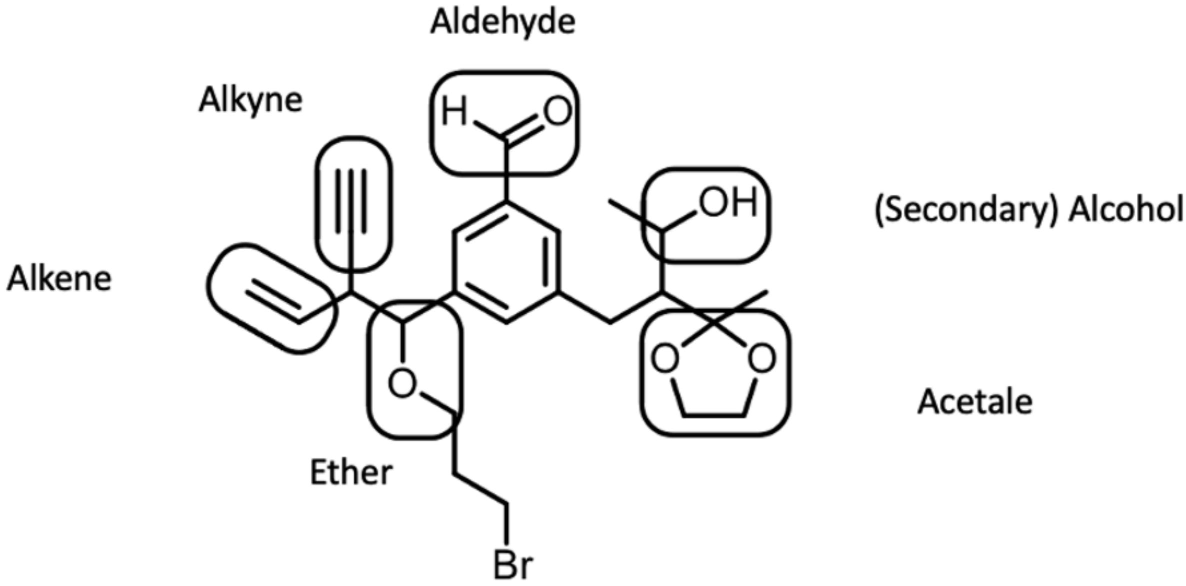
$HO-CH_2-CH_2-OH$





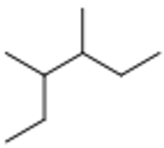
1.2 Functional Groups

Indicate the substance class associated with the circled functional groups.

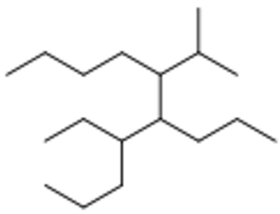


1.3 Nomenclature

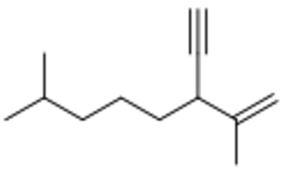
a) Name the following molecules:



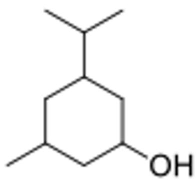
3,4-Dimethylhexan



4-Ethyl-6-isopropyl-5-propyldecan

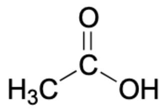


3-Ethinyl-2,7-dimethyloct-1-en

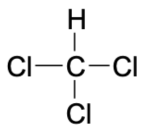


3-Isopropyl-5-methylcyclohexan-1-ol
or
5-Methyl-3-(1-methylethyl)cyclohexan-1-ol

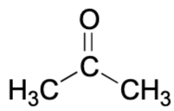
b) Give IUPAC names for acetic acid, chloroform, and acetone.



acetic acid



chloroform



acetone

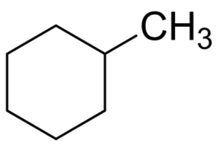
acetic acid: ethanoic acid

chloroform: trichloromethane

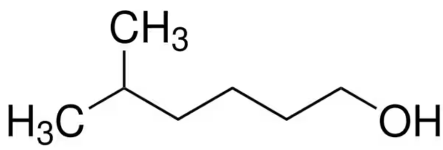
acetone: propanone (not 2-propanone, because the '2' in this case would be redundant: if the carbonyl carbon were not in the #2 position, the compound would be an aldehyde not a ketone)

c) Draw line structures of the following compounds:

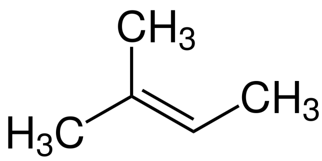
i. Methylcyclohexane



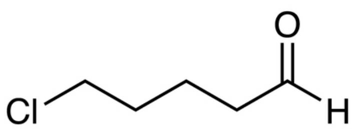
ii. 5-methyl-1-hexanol



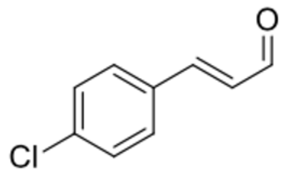
iii. 2-methyl-2-butene



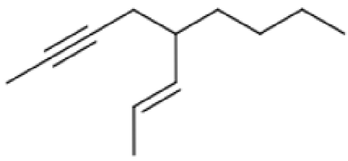
iv. 5-chloropentanal



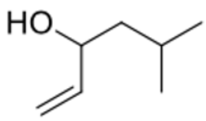
v. (2E)-3-(4-Chlorphenyl)prop-2-en-1-al



vi. (E)-4-Butyloct-6-in-2-en

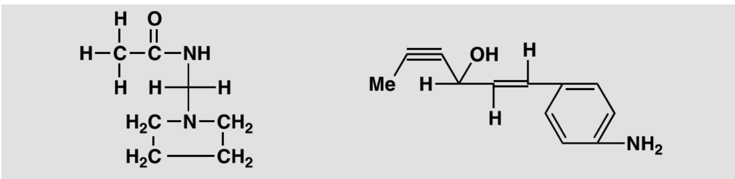


vii. 5-methylhex-1-en-3-ol



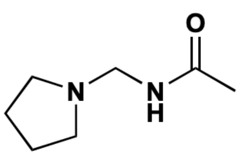
1.4 Structure representation

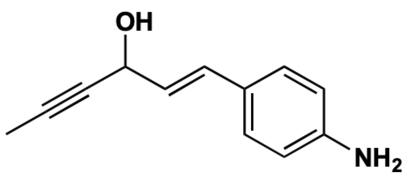
a) What is wrong with these structures? Suggest better ways to represent these molecules [Source: Clayden, Organic Chemistry]



Purpose of the problem: To shock you with two dreadful structures and to try to convince you that well drawn realistic structures are more attractive to the eye as well as easier to understand and quicker to draw.

Suggested solution: The bond angles are grotesque with square planar saturated carbon atoms, bent alkynes with 120° bonds, linear alkenes with bonds at 90° or 180°, bonds coming off a benzene ring at the wrong angles and so on. If properly drawn, the left hand structure will be clearer without the hydrogen atoms. Here are better structures for each compound but you can think of many other possibilities.

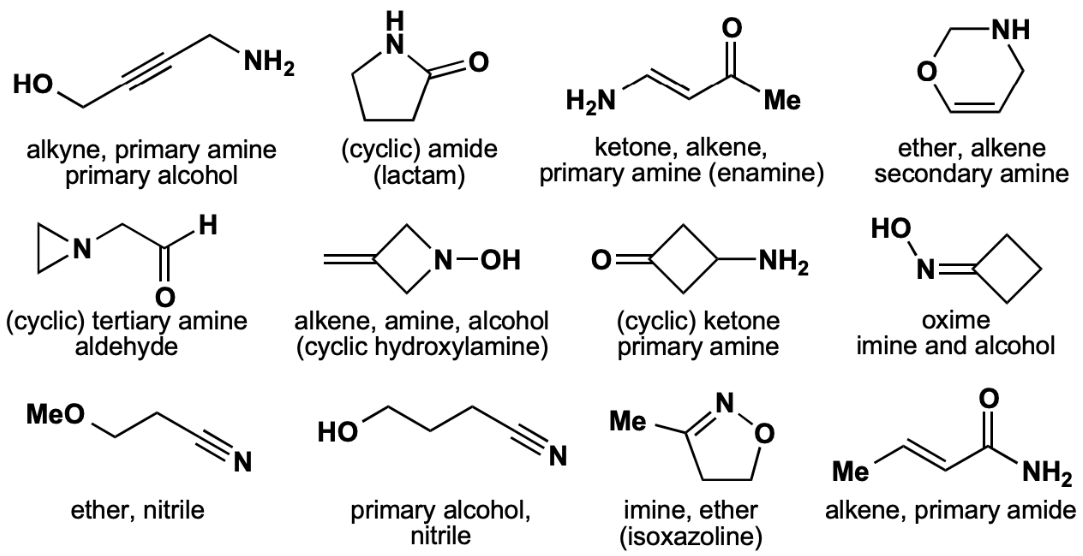




b) Suggest at least four different structures that would fit the formula C_4H_7NO. Show good representations of each one and say which functional groups are present. [Source: Clayden, Organic Chemistry]

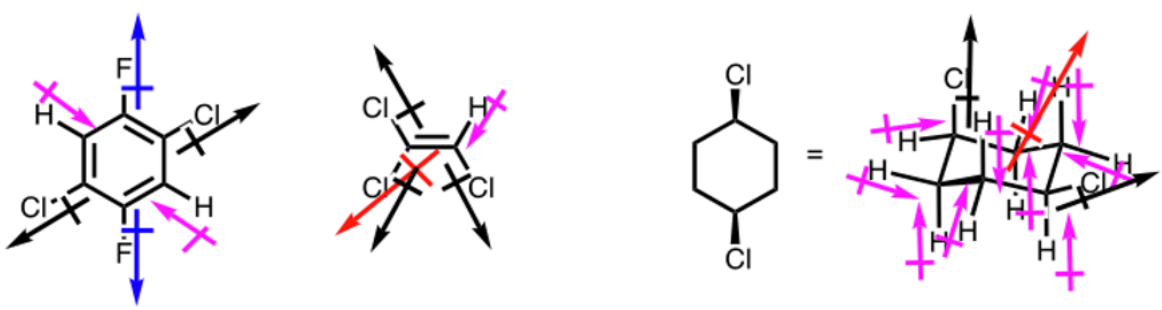
Purpose of the problem: The identification and naming of functional groups is more important than the naming of compounds, because the names of functional groups tell you about their chemistry. This was your chance to experiment with different groups and different carbon skeletons and to experience the large number of compounds you could make from a formula with few atoms.

Suggested solution: We give twelve possible structures – there are of course many more. You need not have used the names in brackets as they are ones more experienced chemists might use.



1.5 Dipole Moment

a) Which of the following molecules have a dipole moment? (Hint: Draw individual bond dipoles first.)



Red = resulting molecular dipole moment. In a), the bond dipole moments cancel each other out. Molecules with an inversion center never have a molecular dipole moment.

b) Which of the following molecules will **not** have a dipole moment?
   A. CH_3Cl
   B. CH_3OCH_3
   C. CH_2Cl_2
   D. CCl_4

1.6 Ionization Potential / Electron affinity / Electronegativity

a) Explain why the Ionization Potential of Hydrogen (H) is higher than that of Lithium (Li).

   The ionization potential of an element indicates the energy required to remove an electron from a neutral atom in the gaseous state. The ionization potential depends on the force of attraction of the atomic nucleus on the electrons. In the case of hydrogen (H), the atom has only one electron in its outermost shell. This electron is strongly attracted to the nucleus because there is only one proton in the nucleus and there are no shielding effects from other electrons. The ionization potential of hydrogen is therefore relatively high.
   In contrast, lithium (Li) has three electrons in its outermost shell. Although the third electron is further away from the nucleus than the electron in hydrogen, it is still shielded by the other two electrons, which reduces the attractive force of the nucleus. This results in a lower ionization potential for lithium compared to hydrogen.
   Coulomb's Law states that the force of attraction between two charged objects (in our case electron & proton) is directly proportional to the product of their charges and inversely proportional to the square of the distance between them. Mathematically expressed, the law is:
   F (attraction force) ~ (q1*q2)/r^2 (r = distance)
   This means that the attraction force between the objects increases as the magnitude of their charges increases and decreases as the distance between them increases.

b) Why do Fluorine bonds have a more ionic character that Chloride bonds, despite Cl having a higher electron affinity than F?

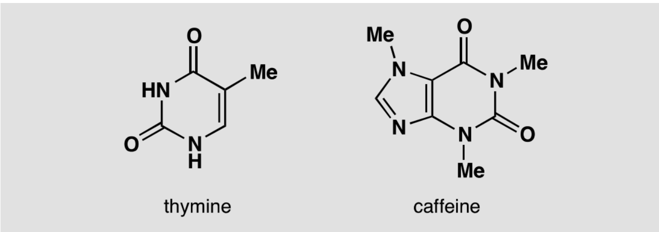
   The determination of the ionic character of a compound relies on the electronegativity difference between the bonding partners. While fluorine (F) has a smaller electron affinity, its smaller radius and consequently higher ionization energy compared to chlorine (Cl) result in a higher electronegativity. Therefore, fluorine compounds exhibit a stronger ionic character than chlorine compounds when bonded to the same partner.

1.7 Aromaticity

a) Which of the following molecules are aromatic, anti-aromatic or non-aromatic?

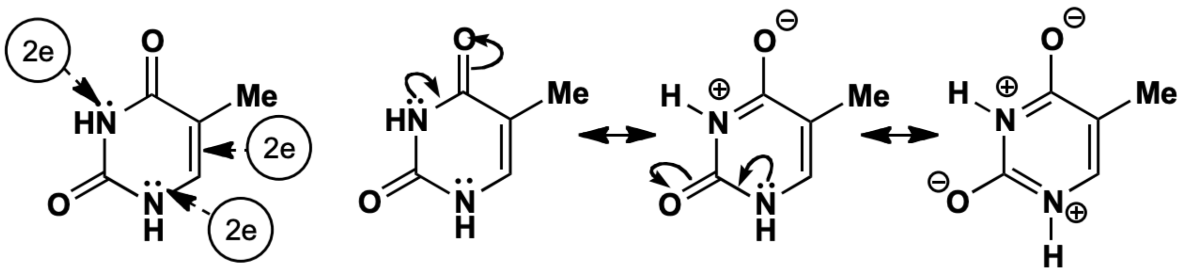
non-aromatic **not-conjugated** **8π electrons**	**anti-aromatic** **8π electrons**	**aromatic** **10π electrons**	**non-aromatic** **not-planar** **10π electrons**
aromatic **6π electrons**	**non-aromatic** **not-conjugated** **12π electrons**	**anti-aromatic** **8π electrons**	**aromatic** **6π electrons**

b) Do you consider that thymine and caffeine are aromatic compounds? Explain. (*Tricky*) [Source: Clayden, Organic Chemistry]



Purpose of the problem: Revision of aromaticity and exploration of the structures of nucleic acid bases.

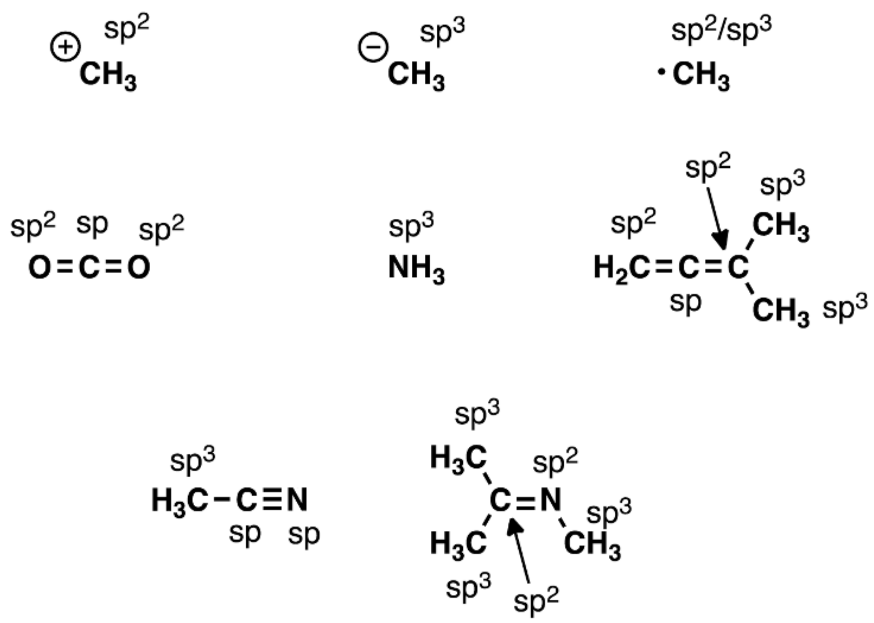
Suggested solution: Thymine, a pyrimidine, has an alkene and lone pair electrons on two nitrogens, making six in all for an aromatic structure. You may have shown this by drawing delocalized structures.



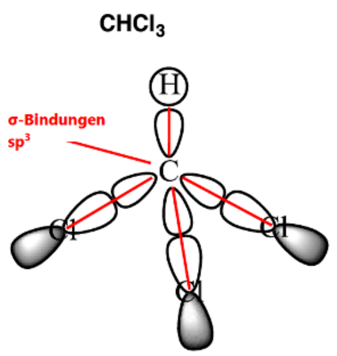
Caffeine, a purine, is slightly more complicated as it has two rings. You might have said that each ring is aromatic if you counted all the lone pairs on nitrogen except those on the ‘pyridine-like’ nitrogen (see p. 741 of the textbook for what we mean here) in the five-membered ring. Or you might have drawn a delocalized structure with ten electrons around its periphery.

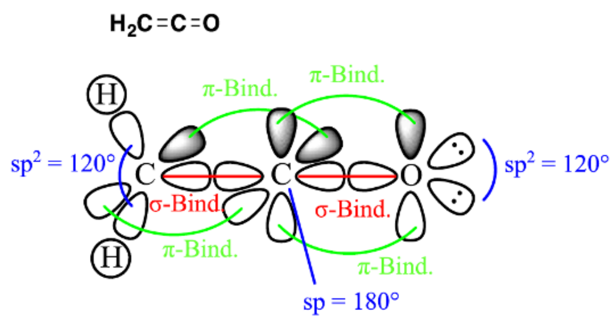
1.8 Hybridization

a) Indicate the hybridization of each nitrogen, oxygen and carbon of the following compounds.



b) Draw all orbitals of the following two molecules and indicate the hybridization, the angles and the type of bond (σ or π).

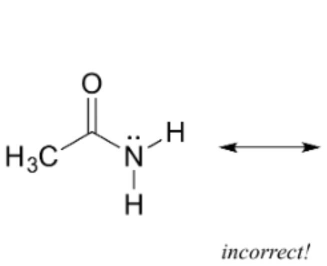


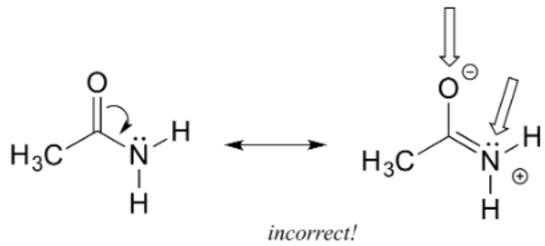


In chloroform, the angle between two Cl atoms (Cl-C-Cl) deviates from the ideal tetrahedral angle. Since the Cl atoms are much larger than the H atom, the angle is 110.4°. Additionally, in CHCl3, the sp3 orbitals of carbon overlap with one of the 3p orbitals of each chlorine atom.

1.9 Resonance

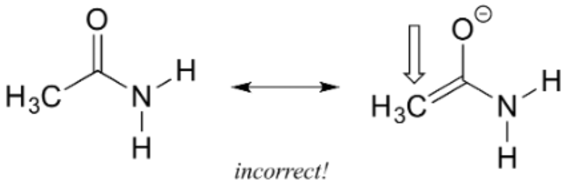
a) Each of the ‘illegal’ resonance expressions below contains one or more mistakes. Explain what is incorrect in each.

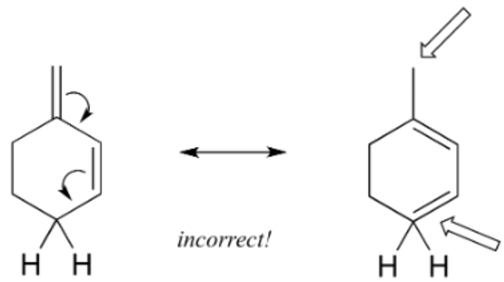




Left: an H atom has been added – in resonance contributors, only pi electrons and lone pairs are rearranged.

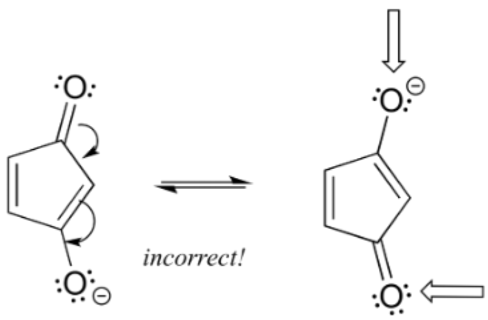
Right: Following the curved arrow, the oxygen atom should have only 6 electrons and thus a positive formal charge. Also the nitrogen is breaking the octet rule (remember that drawing lone pairs is optional, so even if they are not drawn you need to assume they are there).

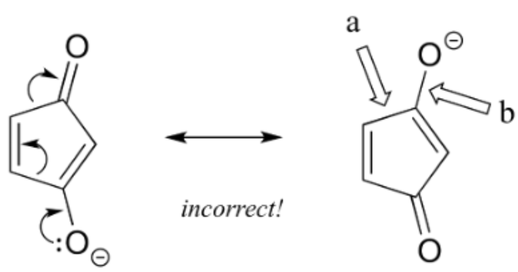




Left: The CH3 carbon is breaking the octet rule with 5 bonds.

Right: One carbon would have a positive formal charge if the arrows are followed, and the other breaks the octet rule with 5 bonds (keep careful track of hydrogen atoms when they are not drawn in line structures!)

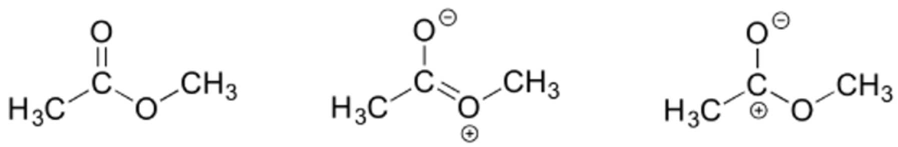




Left: One oxygen should have a positive formal charge, and one breaks the octet rule.

Right: a) the arrow shows this single bond breaking – you can’t break single bonds in a resonance contributor. b) the arrow shows a triple bond forming here, which would also mean the oxygen is breaking the octet rule.

b) Draw three resonance contributors of methyl acetate (an ester with the structure CH_3COOCH_3), and order them according to their relative importance to the bonding picture of the molecule. Explain your reasoning.



The contributor on the **left** is the most stable: there are no formal charges. The contributor in the **middle** is intermediate stability: there are formal charges, but all atoms have a complete octet. The contributor on the **right** is least stable: there are formal charges, and a carbon has an incomplete octet.

1.10 Biomolecules

a) (True/False) Aldehydes, amides, carboxylic acids, esters, and ketones all contain carbonyl groups.

b) By definition, carbohydrates contain which elements?

A. carbon and hydrogen
B. carbon, hydrogen, and nitrogen
C. carbon, hydrogen, and oxygen
D. carbon and oxygen

c) Monosaccharides may link together to form polysaccharides by forming which type of bond?

A. hydrogen
B. peptide
C. ionic
D. glycosidic

d) Microorganisms can thrive under many different conditions, including high-temperature environments such as hot springs. To function properly, cell membranes have to be in a fluid state. How do you expect the fatty acid content (saturated versus unsaturated) of bacteria living in high-temperature environments might compare with that of bacteria living in more moderate temperatures?

In high-temperature environments such as hot springs, bacteria face the challenge of maintaining optimal membrane fluidity. To adapt to these extreme conditions, bacteria living in such environments are likely to have a higher proportion of saturated fatty acids compared to those living in more moderate temperatures. Saturated fatty acids tend to increase membrane rigidity and stability, which can help counteract the excessive fluidity induced by high temperatures. Additionally, bacteria in high-temperature environments may also possess higher levels of branched chain iso-fatty acids. These iso-fatty acids contribute to membrane stability by promoting ordering of hydrocarbon chains, thus helping to maintain membrane integrity under extreme heat. Moreover, it's possible that bacteria in hot environments might have a lower proportion of unsaturated fatty acids compared to those in moderate temperatures. Unsaturated fatty acids, particularly cis-unsaturated ones, are more prone to oxidation and lipid peroxidation, which could be exacerbated in high-temperature conditions. Therefore, reducing the presence of unsaturated fatty acids may help mitigate oxidative damage to the membrane lipids. Overall, bacteria inhabiting high-temperature environments are likely to have membrane compositions skewed towards saturated and branched chain fatty acids, which enhance membrane stability and integrity, thus facilitating their survival and proper functioning in these extreme conditions.

Source: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5487899/

e) Which of the following groups varies among different amino acids?

A. hydrogen atom
B. carboxyl group
C. *R* group
D. amino group