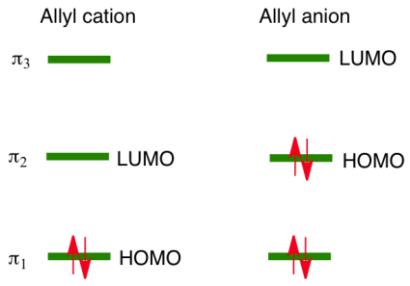
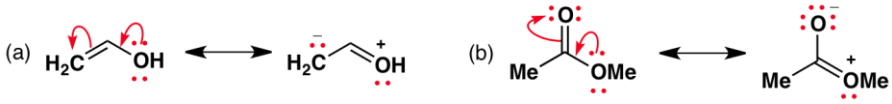
Solutions to Exercises, Chapter 5

5.1 Conjugated systems: (a), (b), (d)

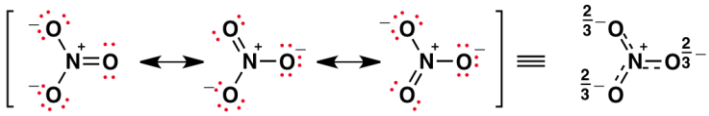
5.2



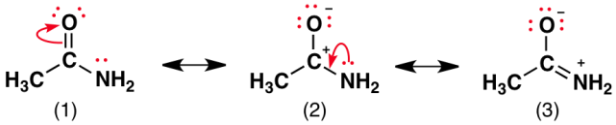
5.3



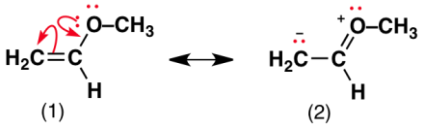
5.4 There are three equivalent resonance contributors, so the three O atoms are equivalent as indicated; it follows that the three bond angles are equal (120°) and the N–O bond lengths are the same.



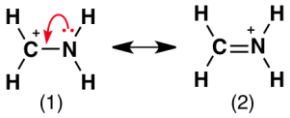
5.5 (a) Resonance contributor (1) is the most important because no charge separation is involved.



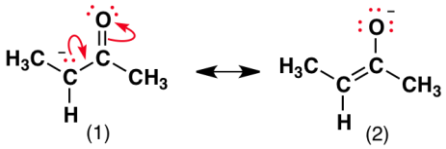
(b) Contributor (1) is more important because of no charge separation being involved.



(c) Contributor (2) is more important because it has more bonds, and the C in (1) has only 6 valence electrons.



(d) Contributor (2) is more important because the negative charge is more stable on the more electronegative O atom.



5.6 Pyridine and pyridinium ion both have three pairs of alternating double and single bonds in a cyclic arrangement. The π MOs are similar to those of benzene (Fig. 5.7) and the electronic configurations are the same (6 π electrons occupying all three bonding MOs). Consequently, both are aromatic: the lone pair on the N of pyridine is orthogonal to the π system in an sp^2 orbital, and its protonation has little effect on the aromaticity.

5.7 (a) Not aromatic due to a cyclic 4 π electron system.

(b) Aromatic with 6 π electrons including the lone pair in a 2p AO on the N.

(c) Aromatic with 6 π electrons of three double bonds.

(d) Not aromatic: the cyclic conjugation is broken by the CH_2.

(e) Not aromatic: the cyclic conjugation is broken by the middle two saturated carbon atoms.

5.8