1.

(a)   There are four core MOs in the carbonate ion because there are four core AOs on the atoms comprising the carbonate ion. (one $1s(C)$ plus three $1s(O)$, one for each oxygen atom).

Because the core MOs do not combine to make bonding or antibonding MOs, they do not affect bond order. Instead, they form nonbonding MOs which closely resemble the AOs from which they were made. As such, it is reasonable to approximate them as part of a core potential.

(b)   A, B, C, D, E, F, H, I, L, N, O, P

These MOs do NOT have a nodal plane passing through all four atoms.

(c)   G, J, K, M

*These MOs have a nodal plane passing through all four atoms.*

(d)   J and K

A degenerate pair of MOs is a pair of MOs with the same energy. You can usually recognize them because they have the same symmetry and the same number of nodes.

(e)   G is bonding

J and K are nonbonding

M is antibonding

(f)   *There are six electrons in pi symmetric MOs. They are highlighted on the resonance structures drawn below:*
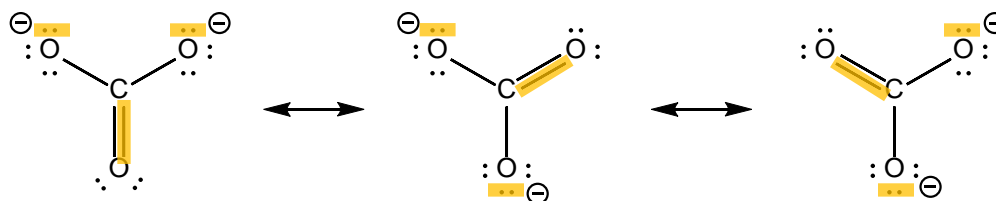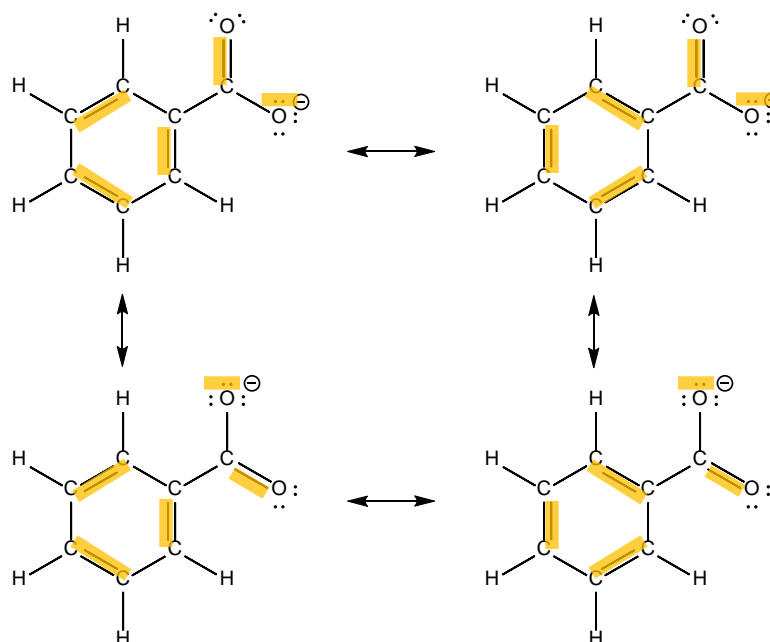

We know from the set of pictures that there are four pi symmetric MOs (though we could also have deduced this from the fact that there are four pi symmetric AOs: $2p_z$ on each atom).

We also know from the answers to (d) and (e) that there are three energy levels: one for a pi bonding MO, one for two pi nonbonding MOs and one for a pi antibonding MO.
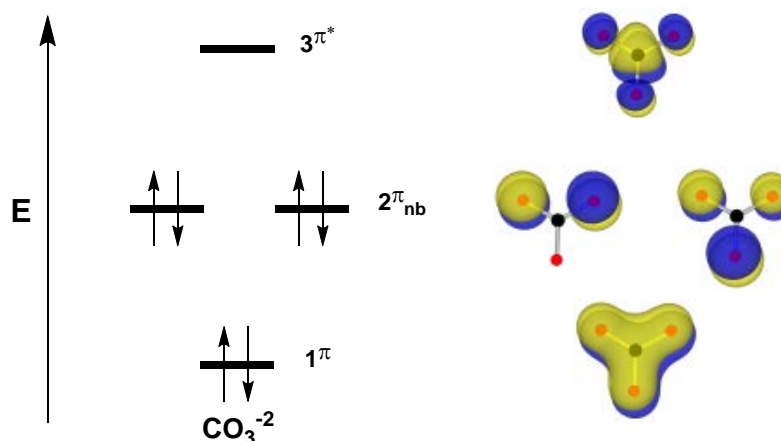
2.

(a)

Highlighting is for part (b).

(b)   i.   41 MOs

total valence MOs = total valence AOs; there are 41 valence AOs in the atoms comprising this ion (1 per hydrogen; 4 per carbon; 4 per oxygen)

     ii.   9 π MOs

This molecule is planar, so each second period atom has one pi symmetric AO (seven $2p_z(C)$ and two $2p_z(O)$) for a total of 9 pi symmetric AOs therefore 9 pi symmetric MOs.

     iii.   32 σ MOs

The MOs which are not pi symmetric are sigma symmetric ($41 - 9 = 32$).

Alternatively, count the sigma symmetric AOs for a total of 32 (five $1s(H)$, seven $2s(C)$, two $2s(O)$, seven $2p_x(C)$, two $2p_x(O)$, seven $2p_y(C)$ and two $2p_y(O)$).
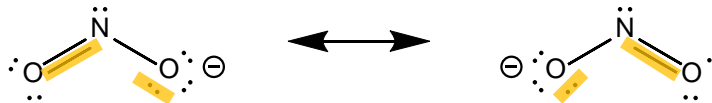
     iv.   36 electrons in σ MOs

The electrons not highlighted in the answer to part (a) are in σ MOs.

     v.   10 electrons in π MOs

The electrons highlighted in the answer to part (a) are in π MOs.

3.

(a)

(b) i. 12 MOs

total valence MOs = total valence AOs; there are 12 valence AOs in the atoms comprising this ion (4 for nitrogen; 4 per oxygen)

ii. 3 π MOs

This molecule is planar, so each atom has one pi symmetric AO (one $2p_z(N)$ and two $2p_z(O)$) for a total of 3 pi symmetric AOs therefore 3 pi symmetric MOs.

iii. 9 σ MOs

The MOs which are not pi symmetric are sigma symmetric ($12 - 3 = 9$).

Alternatively, count the sigma symmetric AOs for a total of 9 (one $2s(N)$, two $2s(O)$, one $2p_x(N)$, two $2p_x(O)$, one $2p_y(N)$ and two $2p_y(O)$).

iv. 14 electrons in σ MOs

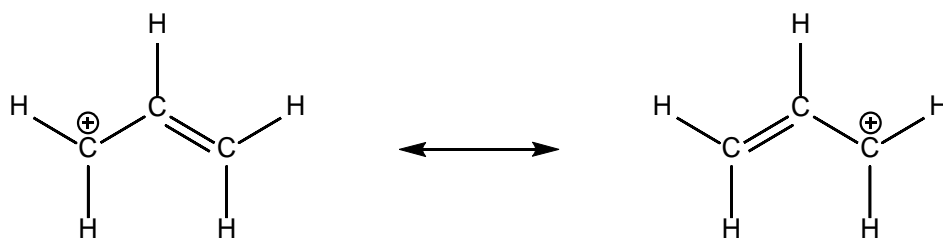*The electrons not highlighted in the answer to part (a) are in σ MOs.*

v. 4 electrons in π MOs

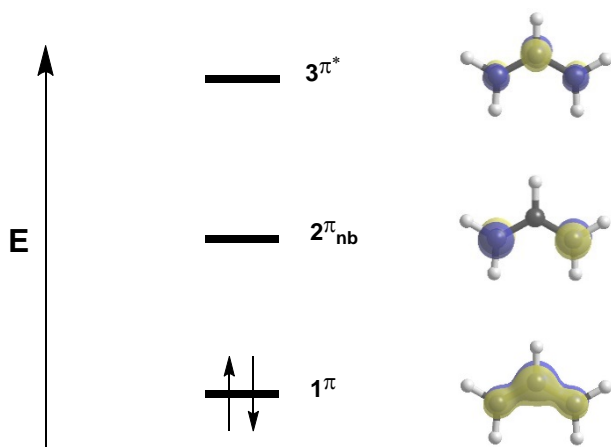*The electrons highlighted in the answer to part (a) are in π MOs.*

(c) i.   π   antibonding

ii. σ   bonding

iii. σ   antibonding

iv. σ   bonding

v.   π   nonbonding

4.

(a)

(b)

E

$3\pi^*$

$2\pi_{nb}$

1π

(c) $C-C$ σ bond order = 1

$C-C$ π bond order $= \frac{1}{2}\left(\frac{2-0}{2}\right) = \frac{1}{2}$

Total $C-C$ bond order $= C-C$ σ bond order $+ C-C$ π bond order $= 1 + \frac{1}{2} = 1.5$

(d) Adding two more π electrons would not change the average $C-C$ bond order.

The additional electrons would be added to $2\pi_{nb}$ which is a nonbonding orbital. Nonbonding electrons do not affect bond order.

5. A π bond has a node along the plane of the molecule. Rotating one of the atoms in the π bond will rotate the orbitals on that atom and break the symmetry required for the π bond. The bond will be broken by twisting it. Thus, twisting a π bond requires enough energy to break the bond (and is therefore difficult to do).

rotate   rotate

molecule A
(*p* orbitals have correct
symmetry to overlap)

pi bond broken!
(*p* orbitals do not have correct
symmetry to overlap)

molecule B
(*p* orbitals have correct
symmetry to overlap)
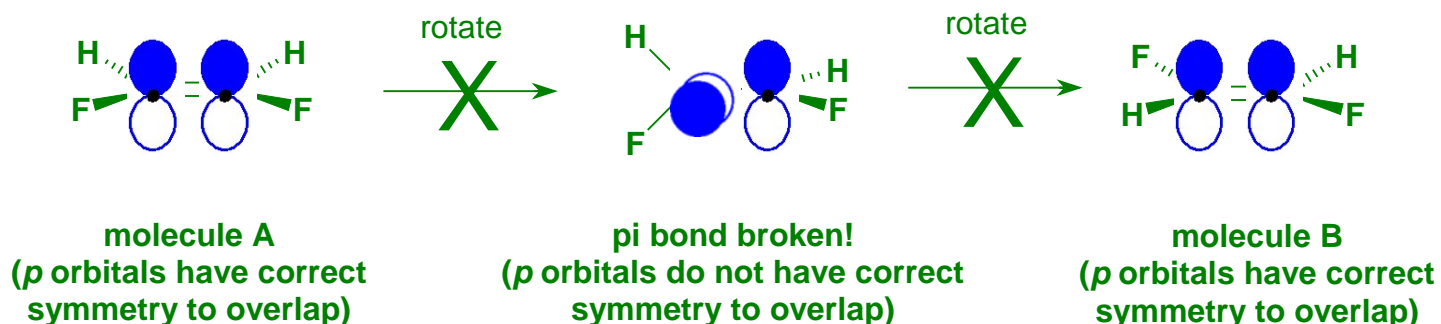
6. While Lewis diagrams make it look like butadiene has two $C = C$ double bonds and one $C - C$ single bond, molecular orbital theory shows that all four carbon atoms share four electrons in pi bonding MOs (in addition to the electrons in sigma MOs).

These pi bonding electrons (particularly the ones in 1π which has density along all three bonds) increase the bond order of the central $C - C$ bond, making that bond shorter and stronger than a typical $C - C$ single bond like the one in butane.
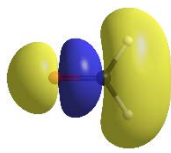
This is best shown by the valence pi molecular orbital energy level diagram below:
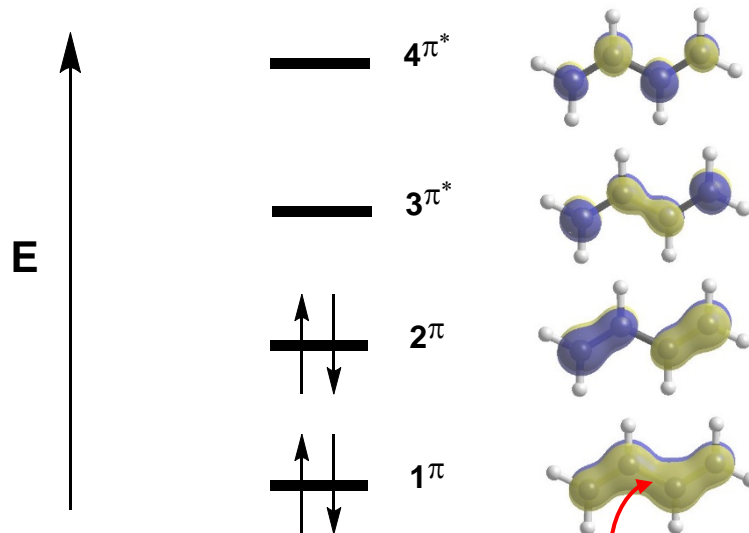
electron density between the two central carbon atoms, increasing the bond order relative to a single bond
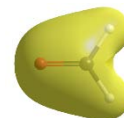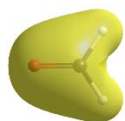
7.

(a)
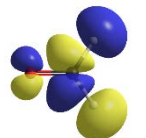
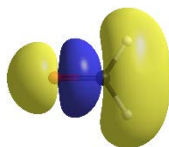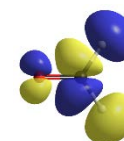bonding   antibonding   bonding

(b)

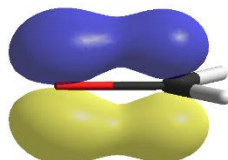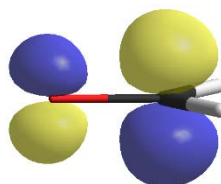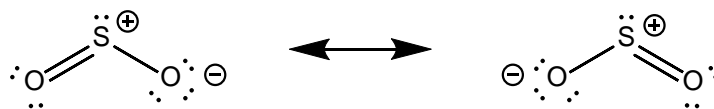lowest energy   middle energy   highest energy

(c)

or

Either answer is fine. The picture on the left shows 1π; the picture on the right shows $2\pi^*$.

In either case, there should be no lobes on the hydrogen atoms since they have no pi-symmetric atomic orbitals to contribute to the pi MOs.
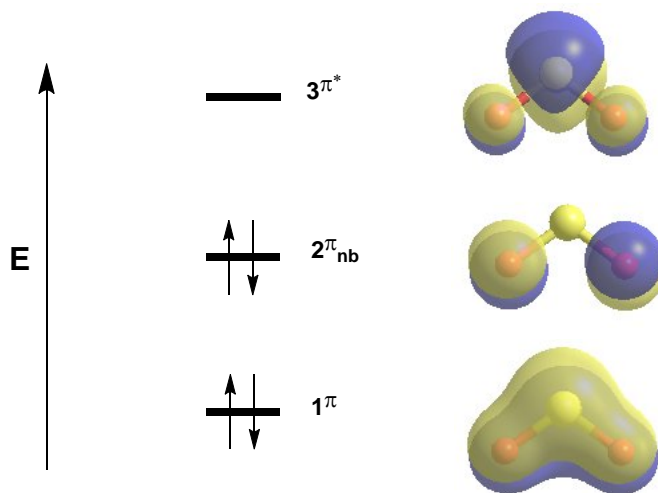
8.

(a) i.

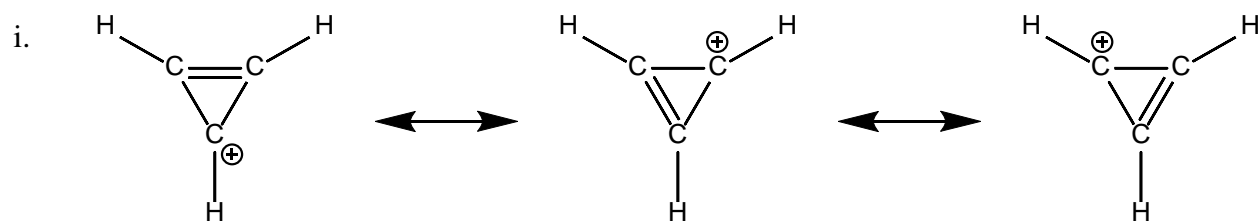ii. $S - O$ bond order $= \frac{2+1}{2} = \frac{3}{2} = 1\frac{1}{2} = 1.5$

(b)

$S - O$ σ bond order $= 1$

$S - O$ π bond order $= \frac{1}{2}\left(\frac{2-0}{2}\right) = \frac{1}{2}$

Total $S - O$ bond order $= S - O$ σ bond order $+ S - O$ π bond order $= 1 + \frac{1}{2} = 1.5$
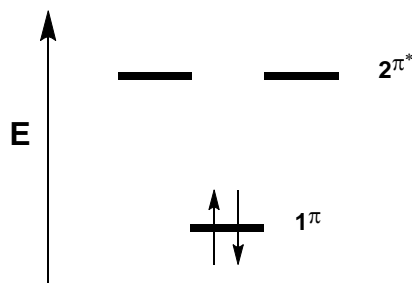
9.

(a)   i.

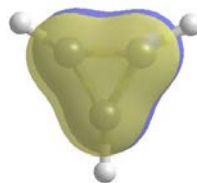ii. $C - C$ bond order $= \frac{2+1+1}{3} = \frac{4}{3} = 1\frac{1}{3}$

(b)   i.

ii. $C - C$ π bond order $= \frac{1}{3}\left(\frac{2-0}{2}\right) = \frac{1}{3}$

iii.   Total $C - C$ bond order $= C - C$ σ bond order $+ C - C$ π bond order $= 1 + \frac{1}{3} = \frac{4}{3} = 1\frac{1}{3}$
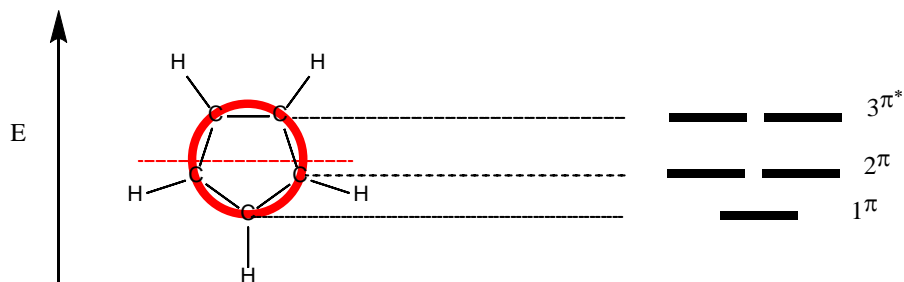
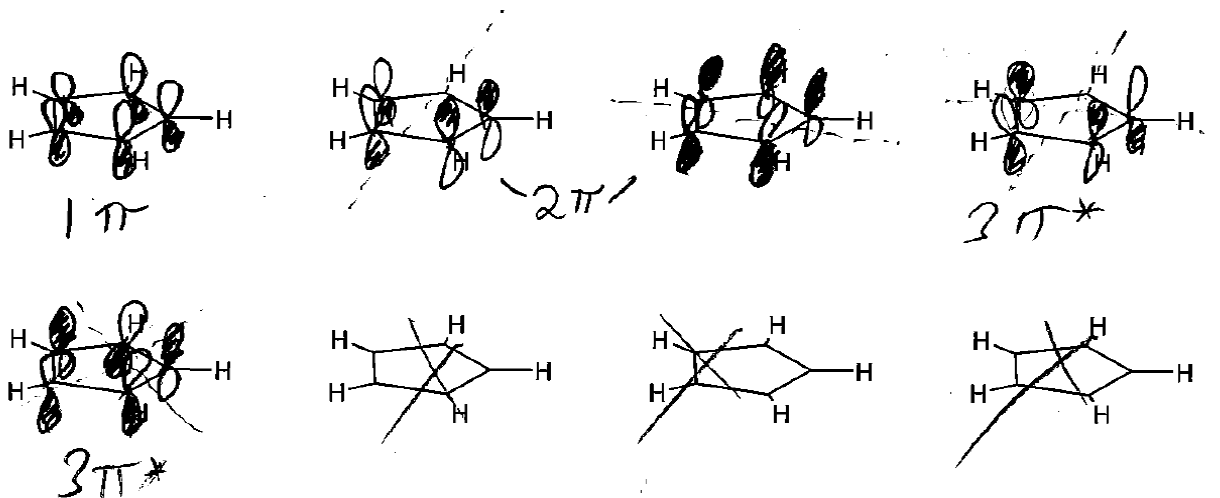(c)   The following picture should be drawn for 1π:

It is understood that your picture may not be as beautiful as the computer-generated image. It should be clear, however, that there is a node in the plane of the page and that there are no other nodes. It should look like the orbital could have been made from three in-phase $2p_z$ orbitals.

10.

(a)

(b)

This instructor chose to draw the set of atomic orbitals combining to make each molecular orbital (instead of drawing the molecular orbital itself). It would also have been perfectly acceptable to draw the five molecular orbitals.

Note the dashed lines showing the perpendicular nodes. Since those were asked for, they were required for full credit.

Answers which did not show relative phase did not get credit.

Answers which had the p orbitals pointing the wrong way did not get credit.

(c) $x = -1$ <u>or</u> $C_5H_5^-$

"Optimal π bonding" means that all of the π bonding MOs are filled but there are no electrons in π antibonding MOs.

To fill all three π bonding MOs requires 6 π electrons. Each carbon atom contributes one π electron, so you need one extra π electron.

An alternative way to look at this is that the sigma skeleton requires 20 electrons. To fill all three π bonding MOs requires 6 π electons, meaning that the species would have a total of 26 valence electrons. Neutral C_5H_5 has 25 valence electrons so $C_5H_5^-$ has 26 valence electrons.
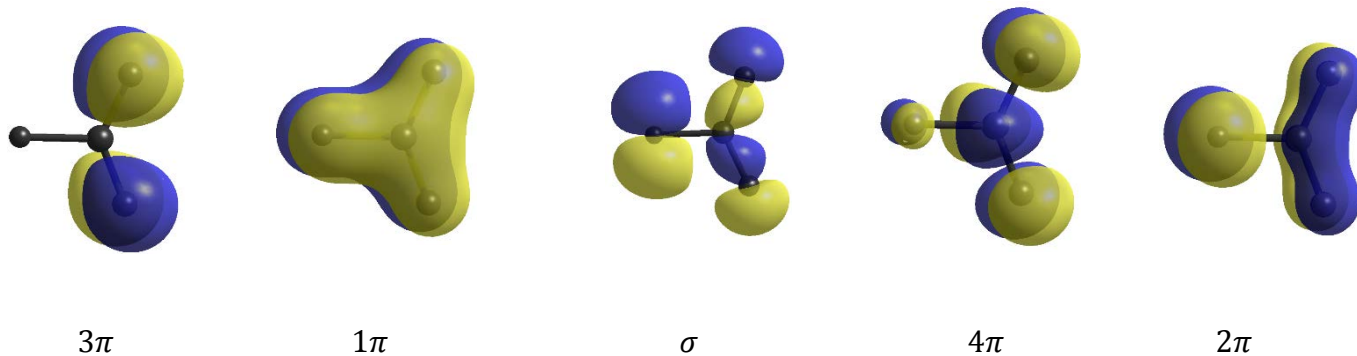
11.

(a)
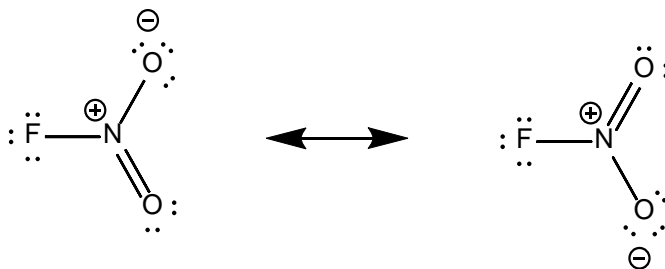
(b) $N - O$ bond order $= \frac{2+1}{2} = \frac{3}{2} = 1\frac{1}{2} = 1.5$

(c)

| 3π | 1π | σ | 4π | 2π |

The pi symmetric MOs have a node in the plane of the molecule. The sigma symmetric MO does not.

The pi symmetric MOs were ranked according to the number of nodes observed: 1π has the fewest nodes; $4\pi^*$ has the most. 2π and $3\pi_{nb}$ both have one perpendicular node, but 2π looks bonding while $3\pi_{nb}$ looks nonbonding, so we would predict the bonding MO to have lower energy than the nonbonding MO.

(d) 1π is made from four p_z orbitals, all combined in-phase (constructively). It is definitely bonding.

2π has constructive overlap along two bonds (the two $N - O$ bonds) and destructive overlap along one bond (the $N - F$ bond). Because there is more constructive overlap than destructive overlap, we can conclude that 2π is bonding.

$3\pi_{nb}$ has no lobes on the central atom. It consists of $2p$ orbitals on the oxygen atoms. Since there is neither constructive nor destructive overlap <u>between orbitals on neighbouring atoms</u>, this MO is neither bonding nor antibonding. So, it must be nonbonding.
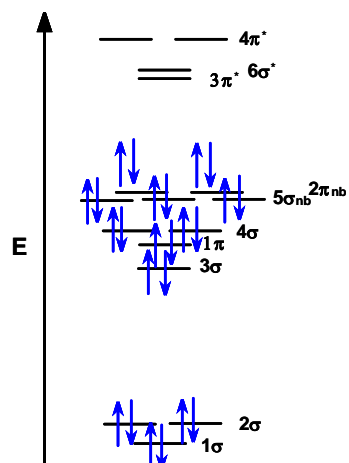
$4\pi^*$ is made from four p_z orbitals, all combined out-of-phase (destructively). It is definitely antibonding.
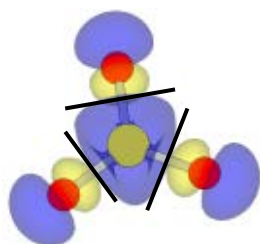
(e) + (f)

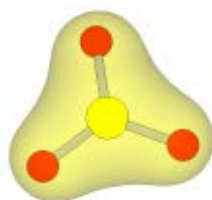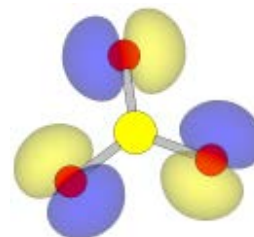$LUMO = 4\pi^*$

$HOMO = 3\pi_{nb}$

12.

(a)

E
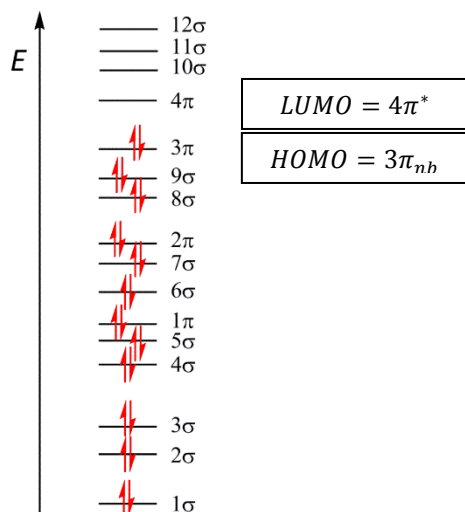
(b)

$6\sigma^*$

antibonding MOs have nodes
between adjacent atoms
(see black lines above)

1σ

bonding MOs have
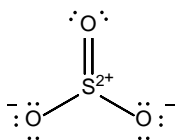electron density between
adjacent atoms (as above)

$5\sigma_{nb}$

many nonbonding MOs look
like atomic orbitals; this MO
looks like $2p$ orbitals on the
oxygen atoms (with no
contribution from sulfur)

(c)

i.

is a better Lewis diagram because when you look at the π MOs only (valence pi molecular orbital energy level diagram), there are two π bonding electrons, four π nonbonding electrons (as well as an empty π^* antibonding MO):
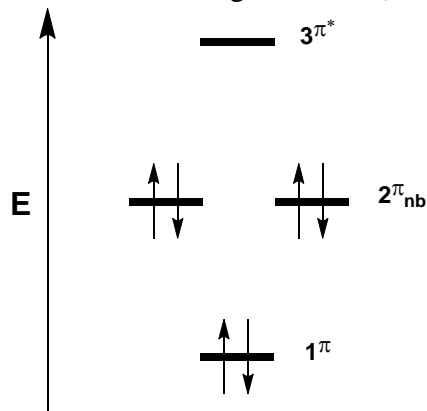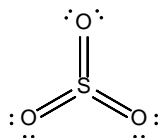

This is consistent with the three pairs of delocalized electrons seen in the resonance structures when sulfur obeys the octet rule:
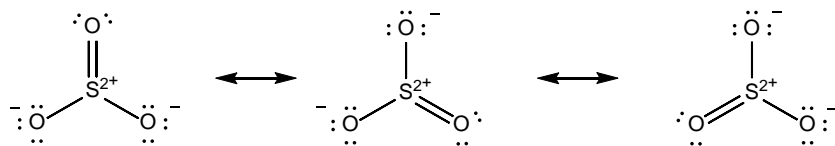
The electrons which move are one bonding pair and two nonbonding pairs. As such, this Lewis diagram does a much better job of showing the delocalization of the π electrons.

ii.

is a better Lewis diagram because the average $S-O$ bond order according to the molecular orbital energy level *(as drawn*)* is $2\frac{1}{3}$.

$$S-O \text{ bond order} = \frac{1}{3}\left(\frac{14-0}{2}\right) = \frac{7}{3} = 2\frac{1}{3}$$

As such, this Lewis diagram does a better job of showing the strength of the $S-O$ bond.

*Some might argue that the 1σ and 2σ MOs are not bonding MOs but are nonbonding MOs from the $2s$ orbitals on the oxygen atoms. This particular calculation showed participation of the $2s$ orbital on sulfur, likely because the energies of the $2s$ orbitals of sulfur and oxygen are within $1\ Ry$ of each other. Photoelectron spectroscopy could be used to determine whether those MOs are truly bonding or nonbonding. (If they were nonbonding instead, the $S-O$ bond order would decrease to $1\frac{1}{3}$.)