

oxygen, as emphasized in the electrostatic potential map shown for acetone. We could come to the same conclusion by recognizing that the C=O bond is polar, with partial positive and negative charges on C and O respectively (as we saw in Section 1.5). Given the insights into bonding orbitals developed in the previous section, we should now be able to use our hybrid VB/MO theory to visualize this polarization. In other words, the σ and π orbitals discussed for ethylene in Section 1.7C should be slightly perturbed for acetone to reflect the polarization in the C=O that is absent in a C=C. Here, only the π bond of C=O will be analyzed, because the lesson for the σ bond is identical.

Figure 1.25 shows the MO theory mixing diagram for the creation of the π and π^* orbitals of C=O. The only difference between this diagram and that of Figure 1.21 is that the energy level of the O $2p$ orbital is placed lower than the C $2p$ orbital. The $2p$ orbitals for O are lower in energy because O is more electronegative than C. In MO theory, when the starting atomic orbitals are not equal in energy, the resulting molecular orbitals most resemble (have a greater contribution from) the atomic orbital that is closest in energy. Hence, the bonding π orbital has a larger contribution from the O, while the antibonding π^* orbital has a larger contribution from the C. Because only the bonding orbital is occupied, the electron density in the bond is concentrated on O. In contrast, in the antibonding orbital, there is considerable orbital character on C, thereby placing a partial positive charge on this atom (a fact that will become important when we start to analyze reactions on C=O groups). Hence, the simple polarization concepts (Section 1.5), the notion of resonance (Section 1.8), and the VB/MO model of bonding (Section 1.7) all lead to the same conclusions.

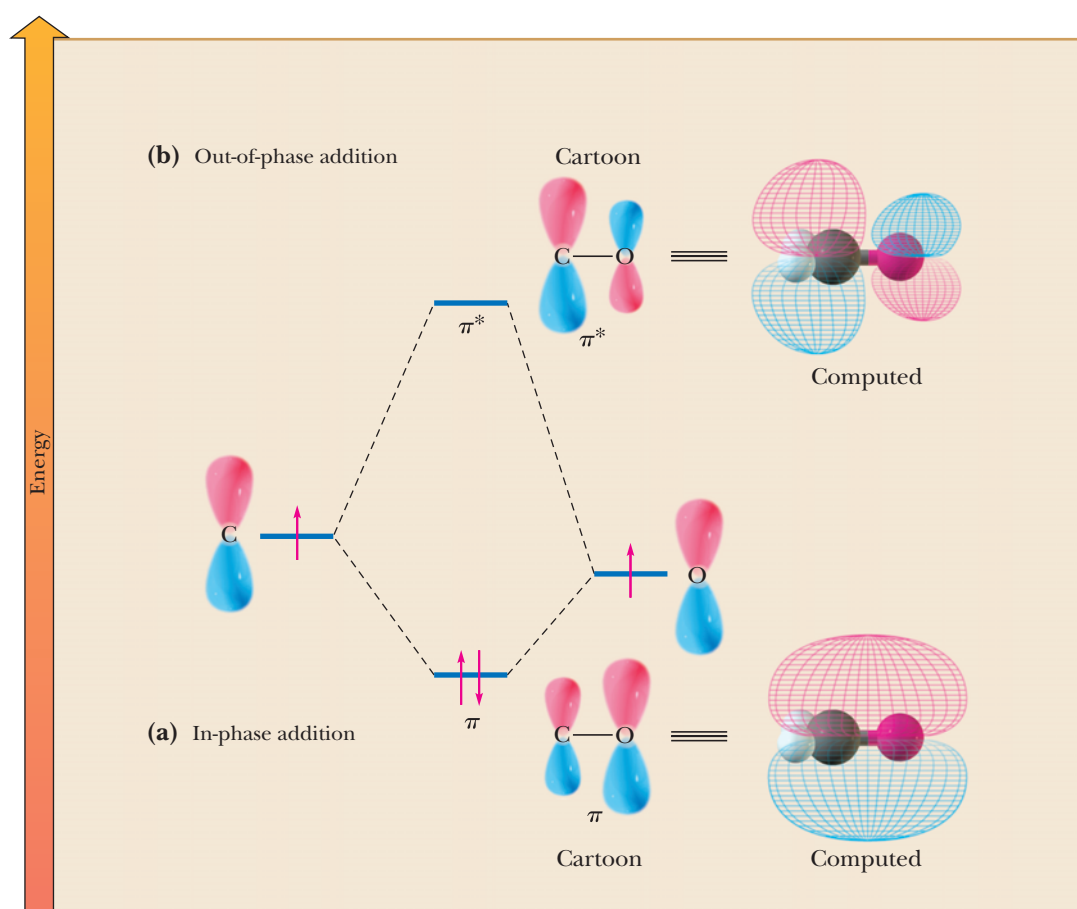


Figure 1.25

Molecular orbital mixing diagram for the creation of any C—O π bond. (a) Addition of two $2p$ orbitals in-phase leads to a π orbital which is lower in energy than the two separate starting orbitals. When populated with two electrons, the π orbital gives a bond that has greater electron density on O compared to C. This is not visually evident in the computed orbital because an O $2p$ orbital is smaller than a C $2p$ orbital. (b) Out of phase addition leads to a π^* orbital that has greater orbital character on C (easily seen in the computed orbital).