

Common, Possible Patterns of Resonance

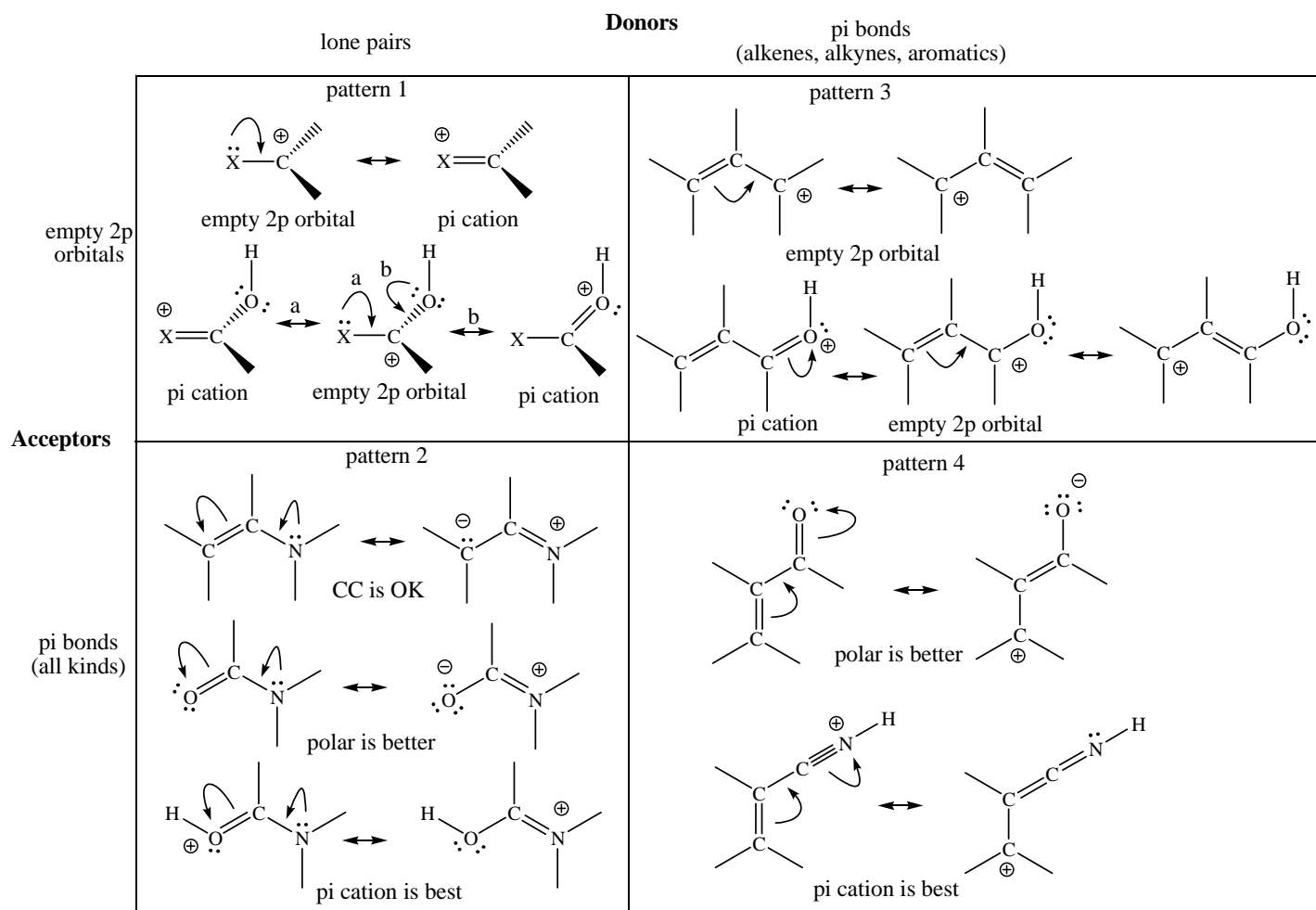
Resonance implies electron delocalization, which is stabilizing because it minimizes electron-electron repulsion. There are four common resonance patterns in organic chemistry, using two donor sites and two acceptor sites. Donor electrons can come from lone pairs and pi bonds. Acceptor sites include an empty 2p orbital (almost always carbon in our course = carbocations) and pi bonds (CC pi bonds are OK, polar is good, pi cations are best). Notice that pi bonds can donate and accept electrons. In our course resonance systems will always occur through p orbitals. There is some overlap among the various patterns depending how they are drawn. Hyperconjugation is a brand of resonance that can use sigma bonds with p orbital, but we will not discuss such resonance.

Resonance Pattern 1 – Lone pair donation (2p orbital) into an empty 2p orbital (carbocation or pi cation).

Resonance Pattern 2 – Lone pair (2p orbital) donation into pi bonds (many kinds, CC, CN, CO, NO, NN, etc.).

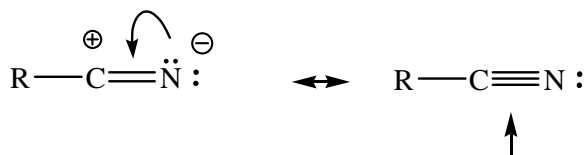
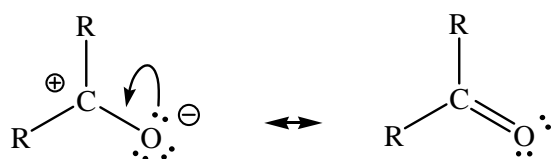
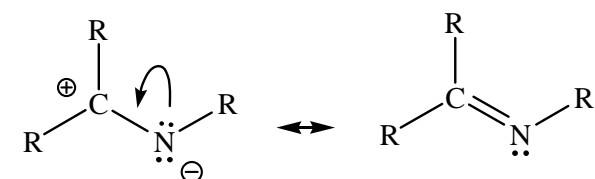
Resonance Pattern 3 – Pi bond donation (from alkene, alkyne or aromatic) into an empty 2p orbital (carbocation or pi cation).

Resonance Pattern 4 – Pi bond donation (from alkene, alkyne or aromatic) into a pi bond acceptor (alkene, alkyne, aromatic, carbonyl, imine, nitrile, etc, polar is good, pi cations are best.)



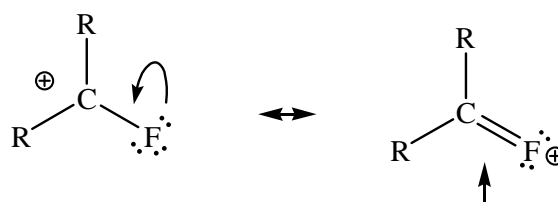
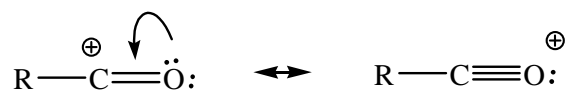
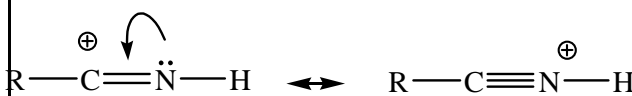
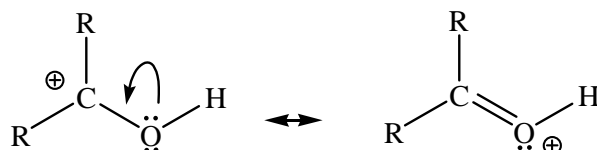
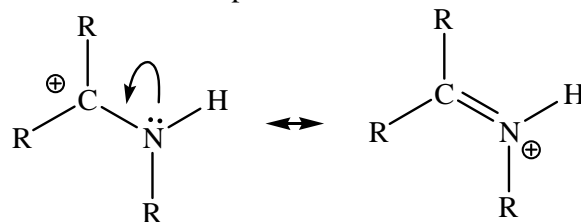
Resonance Pattern 1 – Lone pair donation into an empty 2p orbital (carbocation or pi cation). This is common in polar pi systems or pi cations (see the example at the bottom of this page).

Usually we write these examples the other way around, starting with the structure having the maximum number of bonds and show the expected polarization forming the minor resonance by pushing the pi electrons to the more electronegative atom. In these examples we are doing it backwards, showing a lone pair sharing with an empty 2p orbital, making a pi bond.



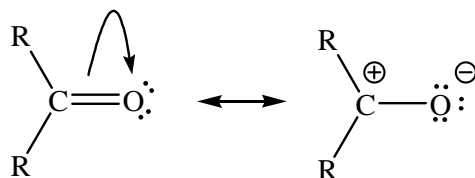
These structures have more bonds and full octets and are considered the major contributor.

pi cations

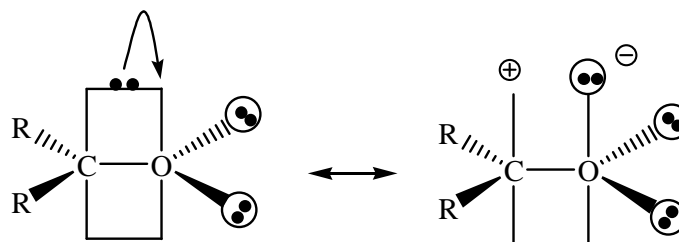


These structures have more bonds and full octets and are considered the major contributor.

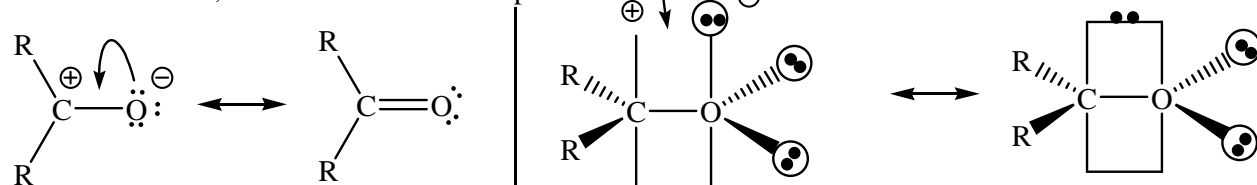
2D resonance structures - carbonyl resonance, this is the usual way of showing carbonyl resonance (reverse of above).



3D resonance structures - carbonyl resonance



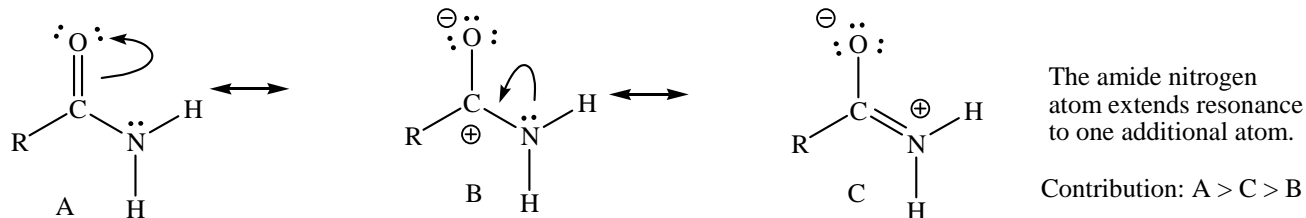
If we turn it around, it shows formation of a pi bond.



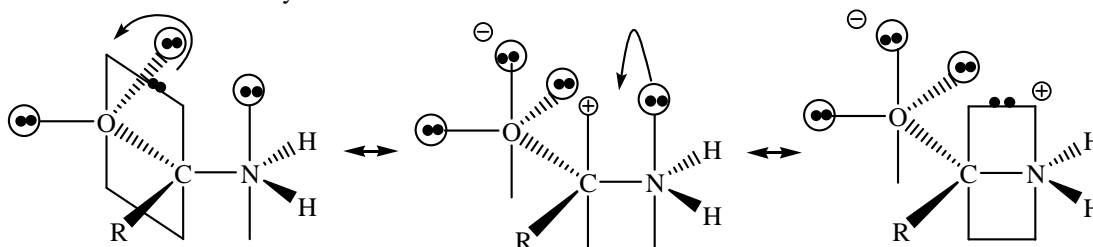
Organic Resonance Systems

Electron donation can occur from 2 or even 3 sides (wherever a lone pair is adjacent to an empty 2p orbital).

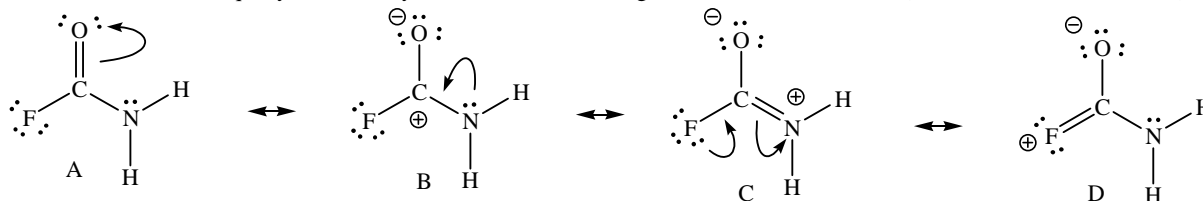
2D resonance structures - carbonyl resonance with one adjacent lone pair



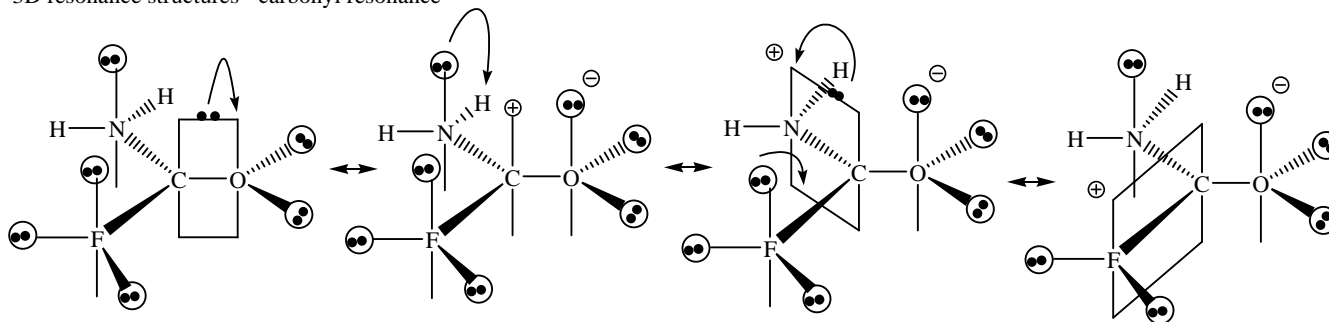
3D resonance structures - carbonyl resonance



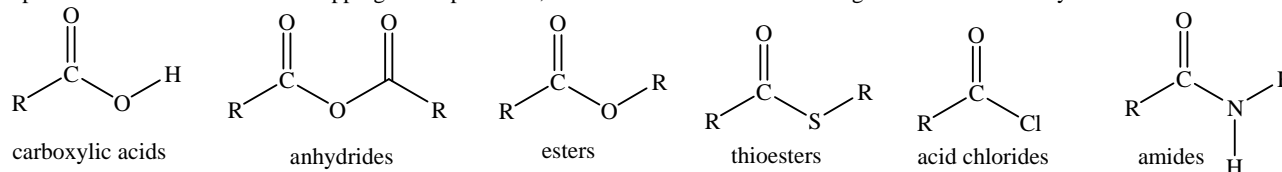
2D resonance structures - carbonyl resonance with two adjacent lone pairs. We judge resonance structures with full octets and more bonds as better, that would be A, C and D below. Because A does not separate charge we judge it to be the best. Nitrogen is a much better electron pair donor than fluorine so C is better than B, but because of its high electronegativity, fluorine's resonance effect is about equally cancelled by its electron withdrawing inductive effect, so $D \approx B$ (contribution: $A > C > D \approx B$).



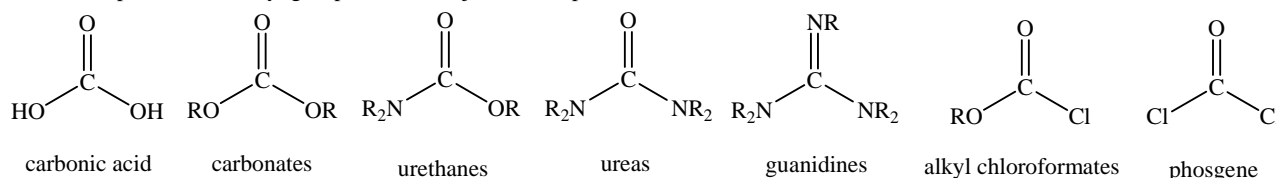
3D resonance structures - carbonyl resonance



A few examples of a carbonyl group with one adjacent lone pair. Lone pair donation is best when all overlapping orbitals are all 2p. Larger 3p orbitals are often shown overlapping with 2p orbitals, but are not as effective at sharing their electron density.

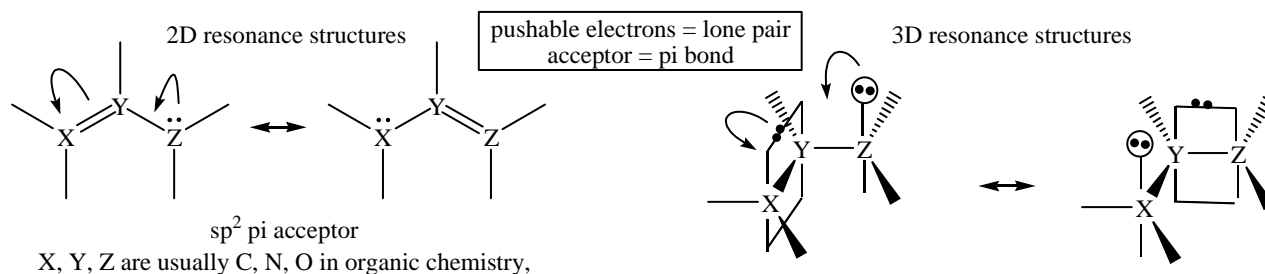


A few examples of a carbonyl group with two adjacent lone pairs.

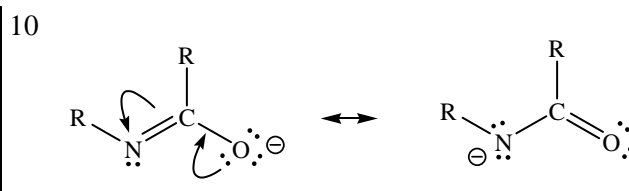
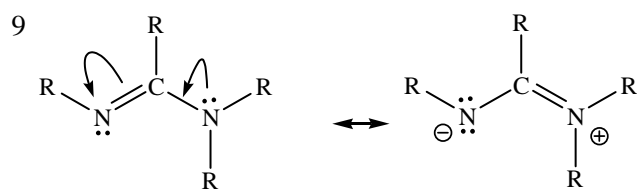
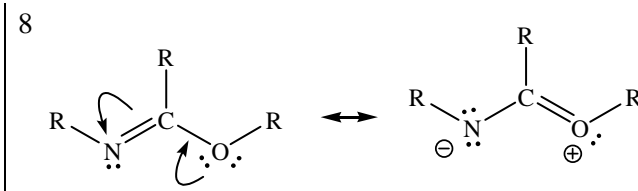
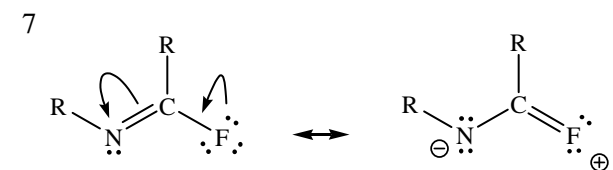
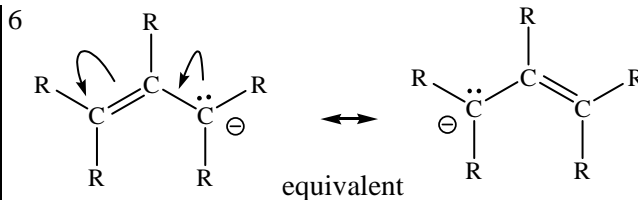
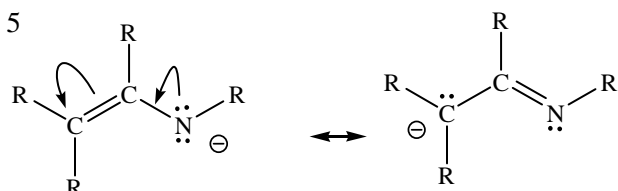
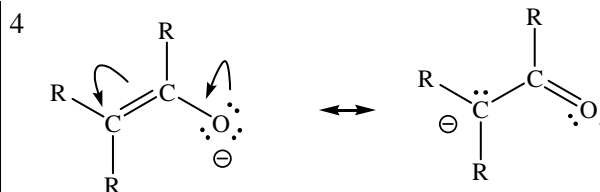
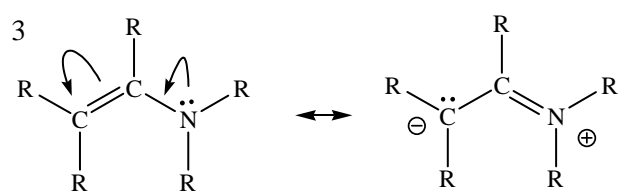
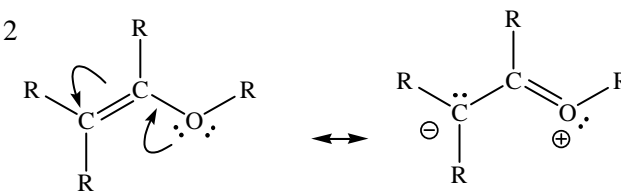
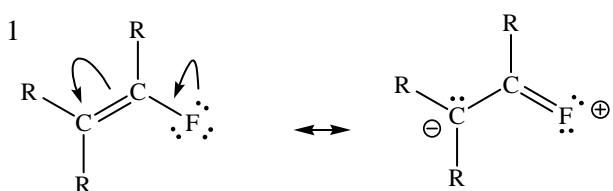


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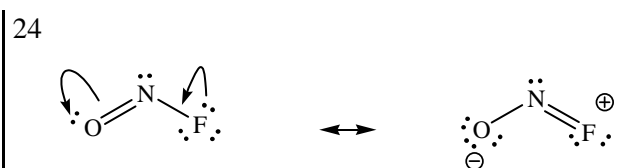
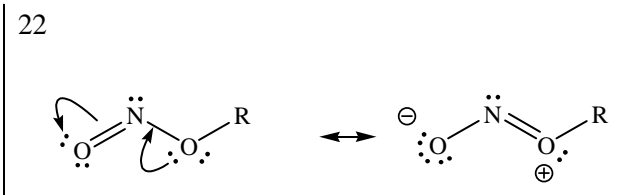
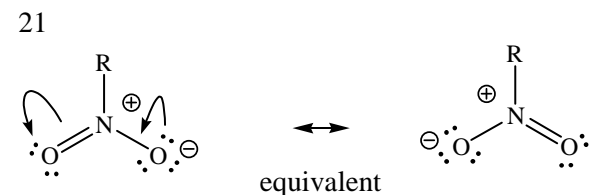
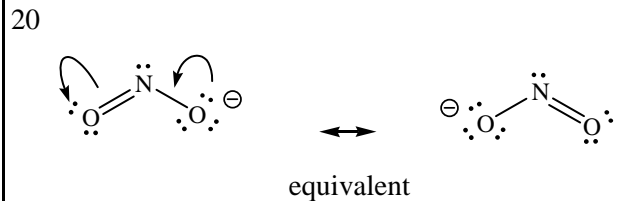
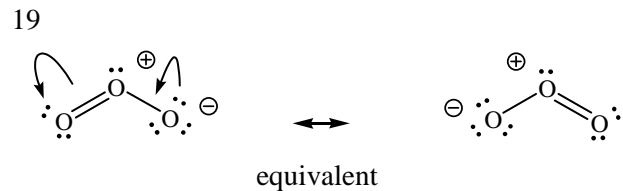
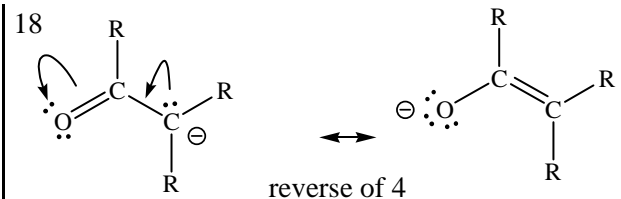
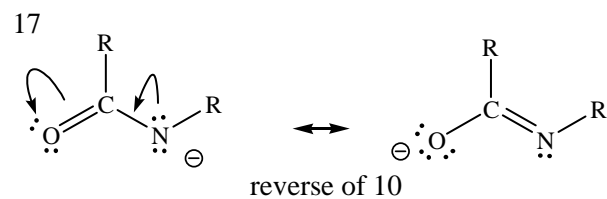
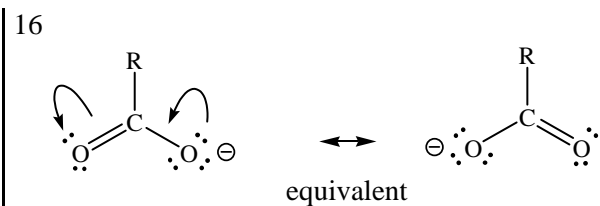
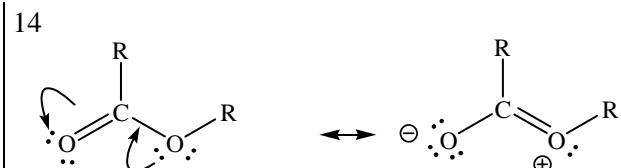
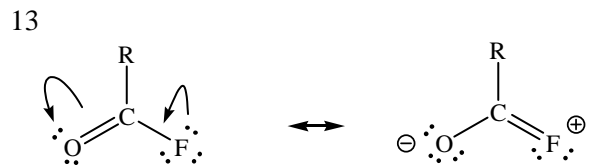
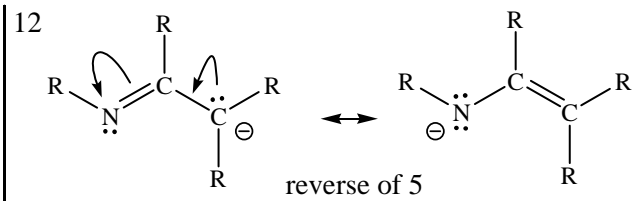
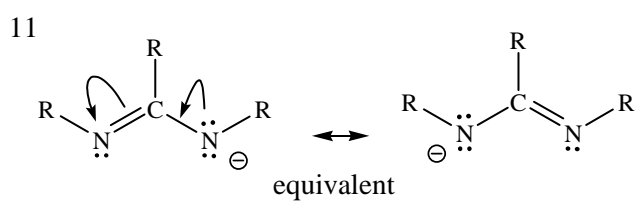
Resonance Pattern 2 – Lone pair donation into pi bonds (many kinds). Formal charge can vary depending on the atoms and number of bonds. Decide an atom's hybridization (shape and bond angles too) using a 2D resonance structure where it has its maximum bonds. Use the 2D structures to decide how to draw the 3D structures. 'R' is an H or carbon group below.



The examples below can be viewed in either direction.

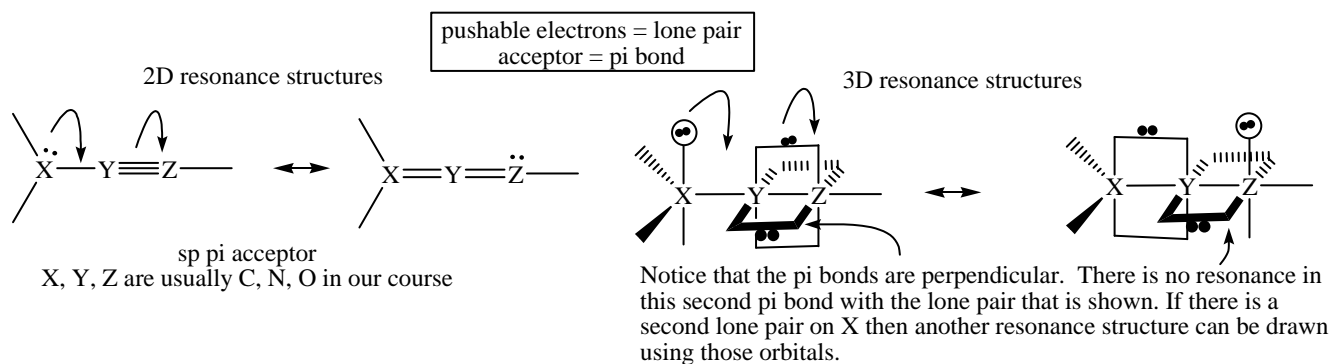


Organic Resonance Systems

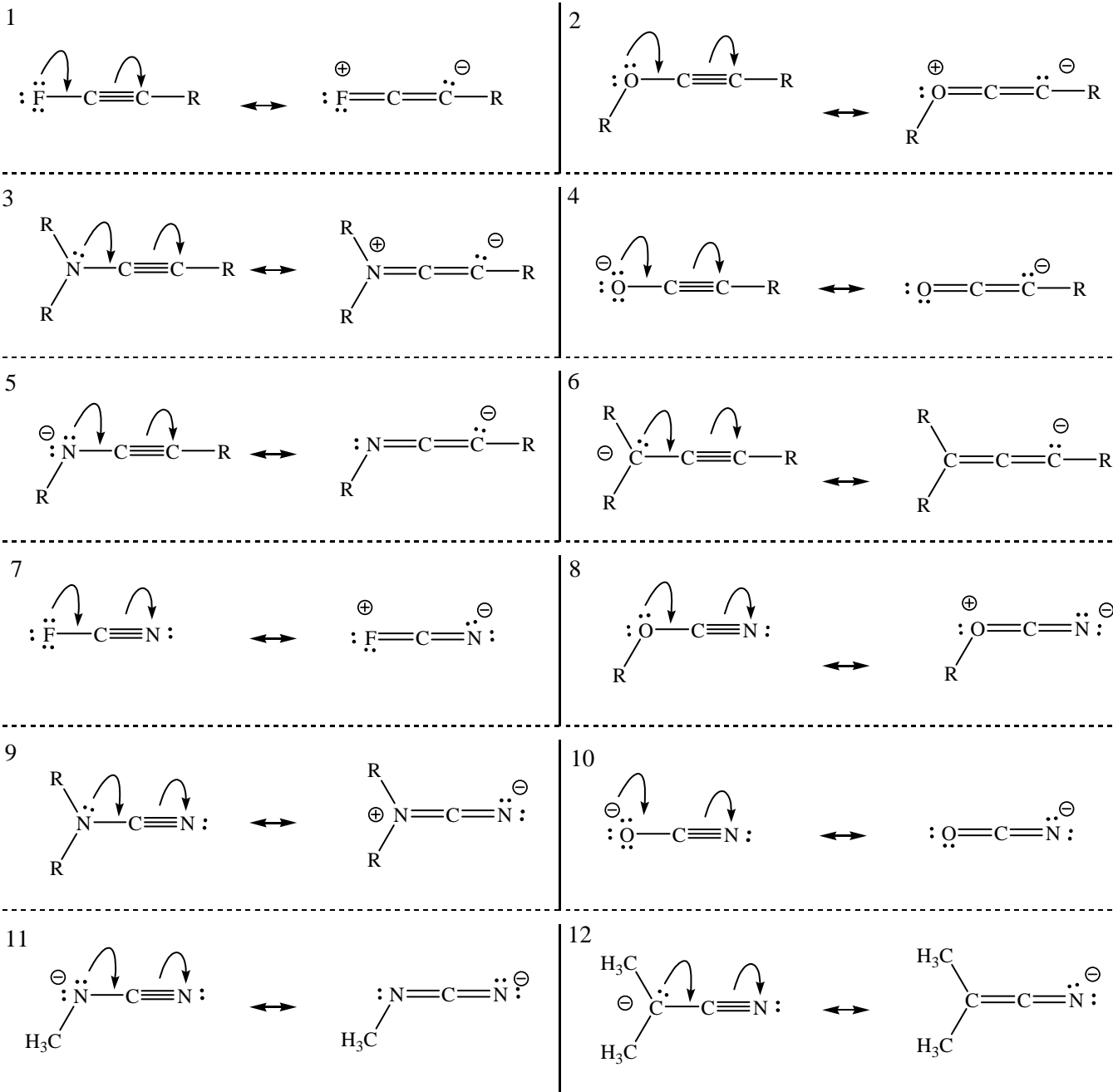


There are even more possibilities! All of the above examples can be written in the reverse direction, and some are.

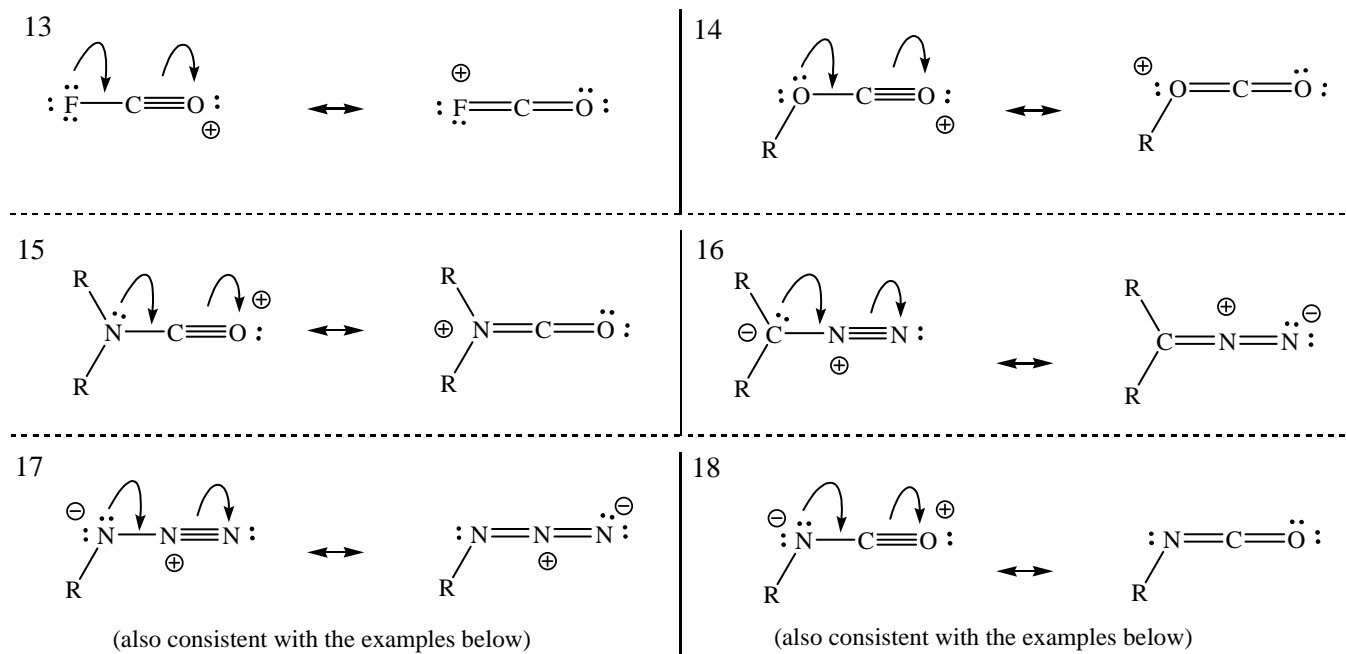
Organic Resonance Systems



The examples below can be viewed in either direction. 'R' is an H or carbon group below.

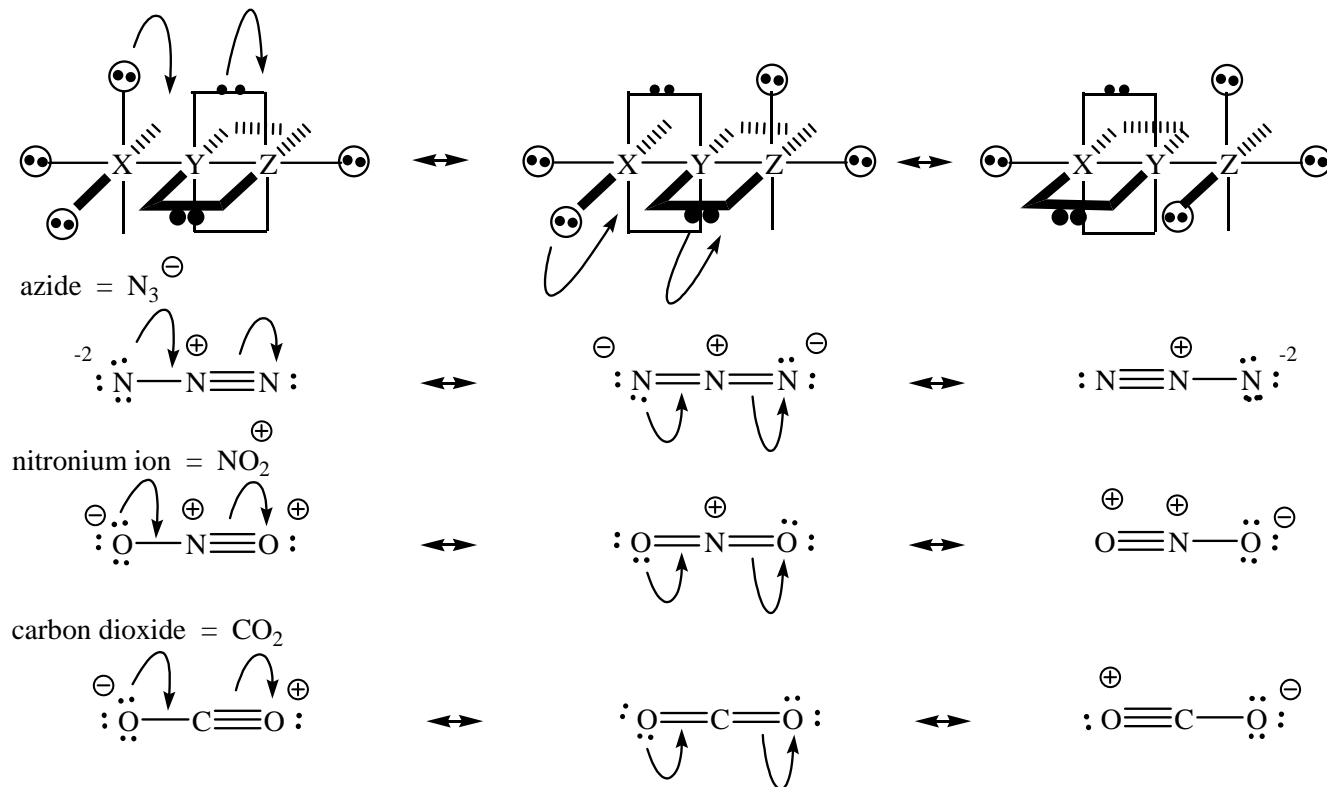


Organic Resonance Systems



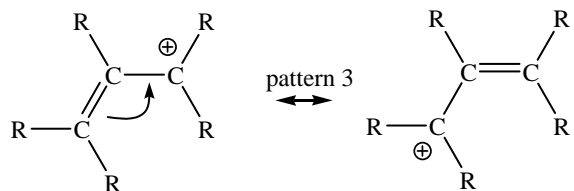
Triple bonds have perpendicular pi bonds. Lone pairs can be parallel to either pi bond, in effect having two independent resonance patterns in the same structure. The middle structures look like the end atoms would be hybridized as sp^2 , but in the first and last structures they look like sp . They can't be both. We assume an atom's hybridization to be consistent with whichever structure shows the most bonds for that atom, in this case sp . Not everyone would write these this way, but sometimes it makes sense.

3D skeleton and resonance structures.

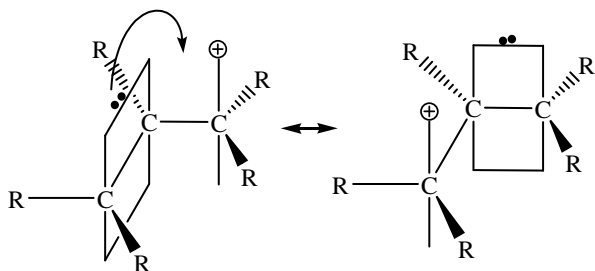


Resonance Pattern 3 – We only show pi bond donation from an alkene, alkyne or aromatic into an empty 2p orbital (carbocation). By spreading out the electrons the positive charge is stabilized. We do not show this sort of resonance using CO or CN pi bonds, assuming that the more electronegative nitrogen and oxygen atoms are not as willing to give away their electrons (less than an octet). The second column (right side) compares pattern 2 with this pattern.

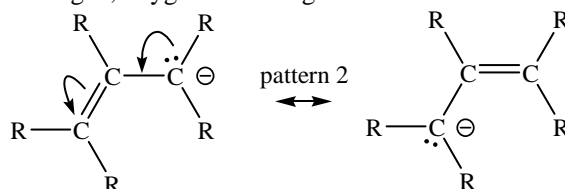
2D Lewis structure alkenes as donors to empty 2p carbocations.



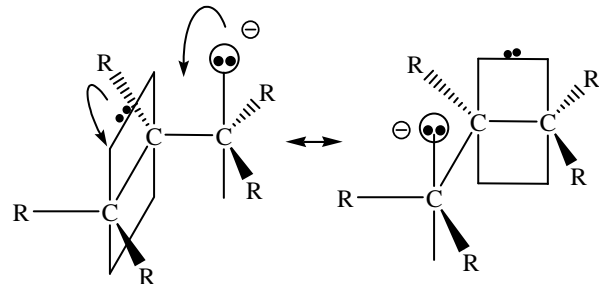
3D Lewis structure



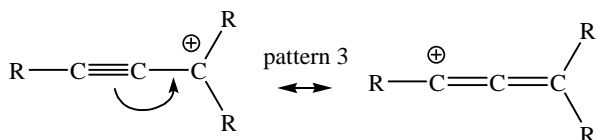
2D Lewis structure alkenes as acceptors (donor atoms can be anions of carbon, nitrogen and oxygen or neutral atoms of nitrogen, oxygen and halogens).



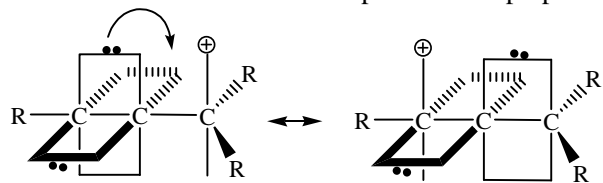
3D Lewis structure



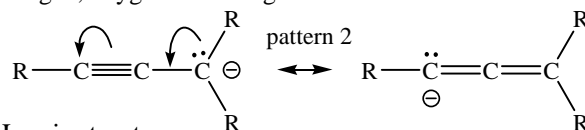
2D Lewis structure alkynes as donors to empty 2p carbocations.



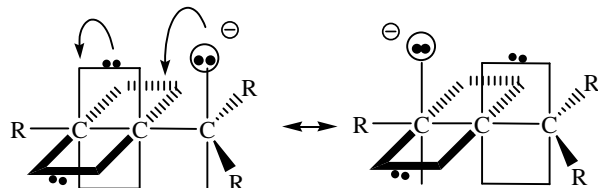
3D Lewis structure - notice the pi bonds are perpendicular



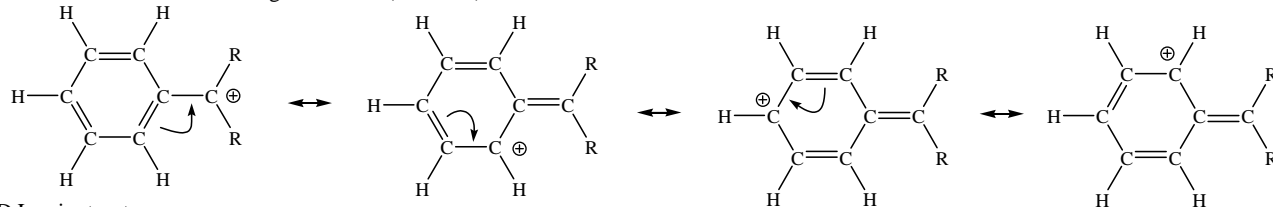
2D Lewis structure alkynes as acceptors (donor atoms can be anions of carbon, nitrogen and oxygen or neutral atoms of nitrogen, oxygen and halogens).



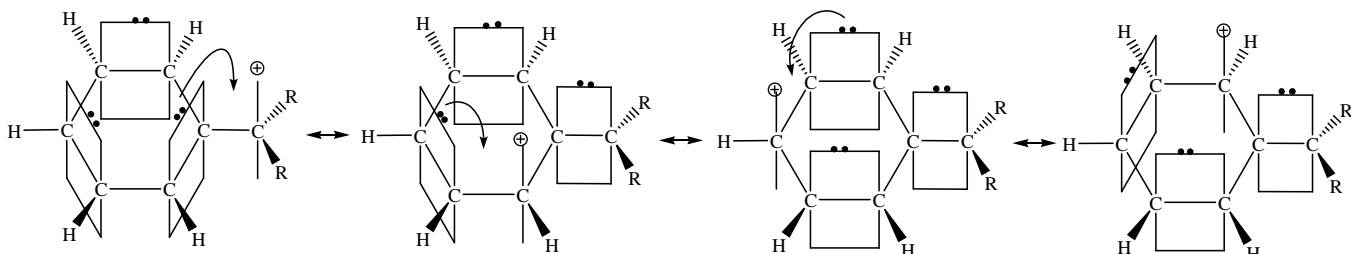
3D Lewis structure



2D Lewis structure aromatic rings as donors (Pattern 3)

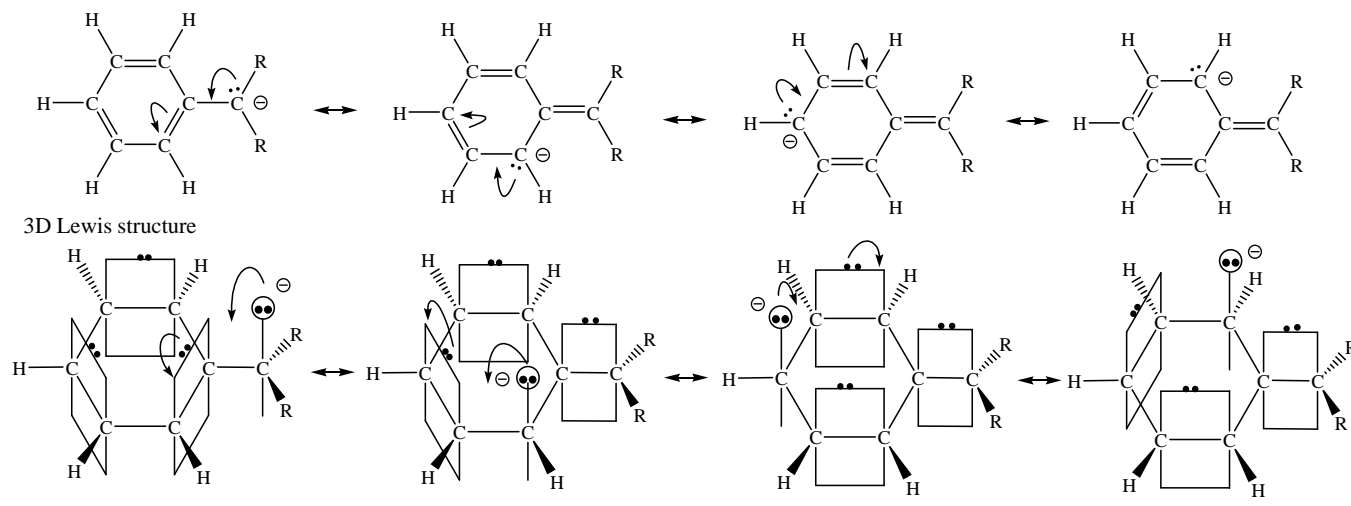


3D Lewis structure



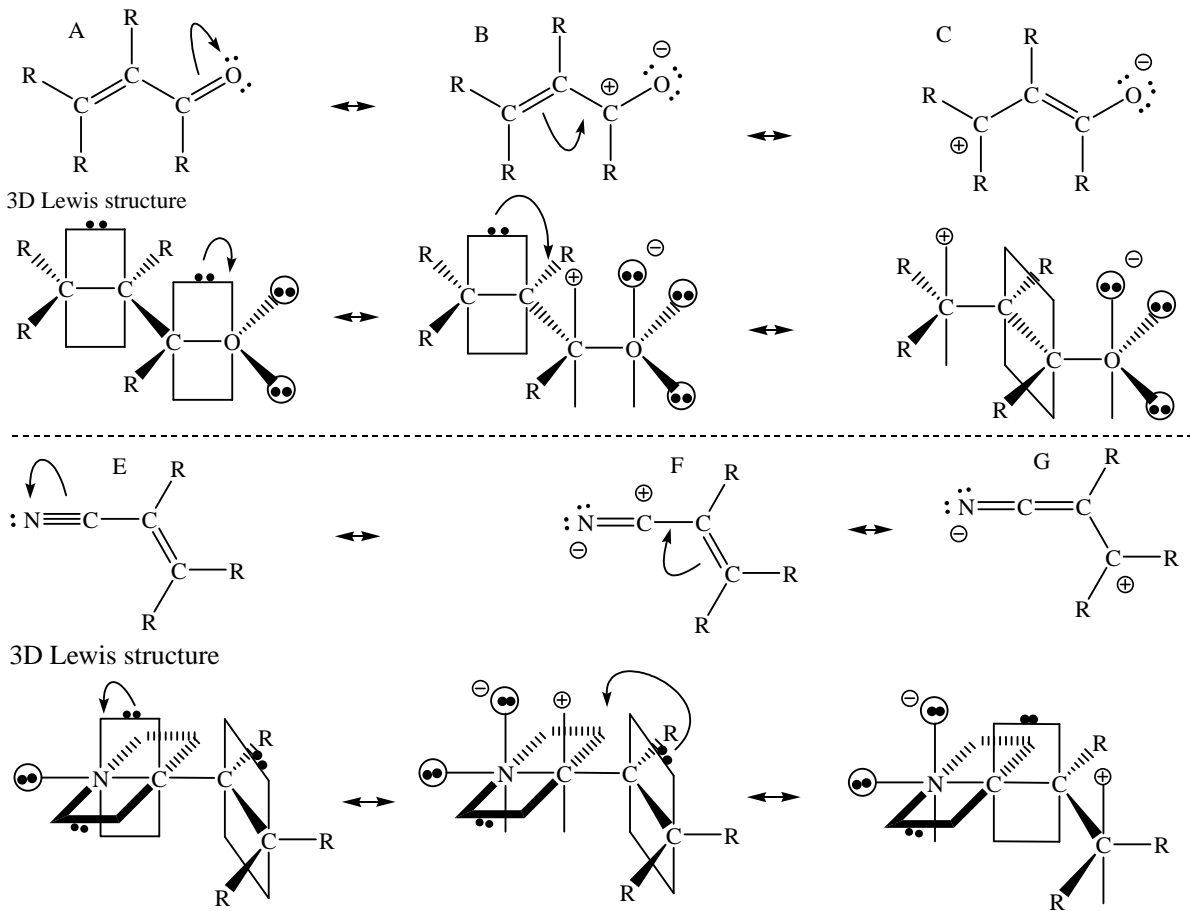
Organic Resonance Systems

2D Lewis structure aromatic rings as acceptors (donor atoms can be anions of carbon, nitrogen and oxygen or neutral atoms of nitrogen, oxygen and halogens. (Pattern 2)



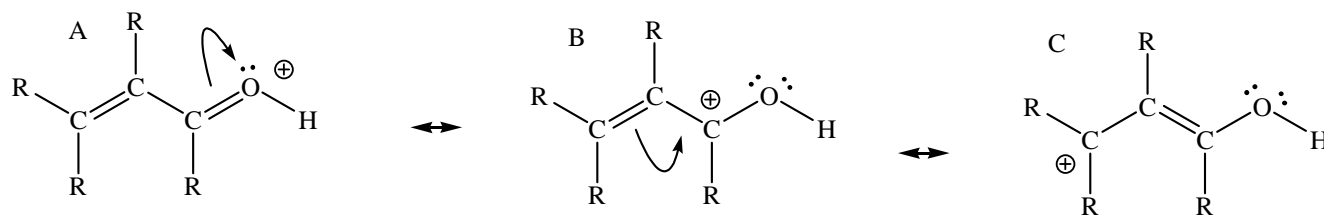
Resonance Pattern 4 – Pi bond donation (from alkene, alkyne or aromatic) into a pi bond acceptor (alkene, alkyne, aromatic, carbonyl, imine, nitrile, etc.). A CC bond is OK, a polar pi bond acceptor is better and a pi cation is the best acceptor.

Neutral pi systems - In resonance pi systems move electrons towards electronegative atoms (oxygen or nitrogen). Notice the partial positive site is spread to multiple centers (two atoms in these examples). Structure A can be shown going directly to C and structure E can be shown going directly to G using 2 arrows.

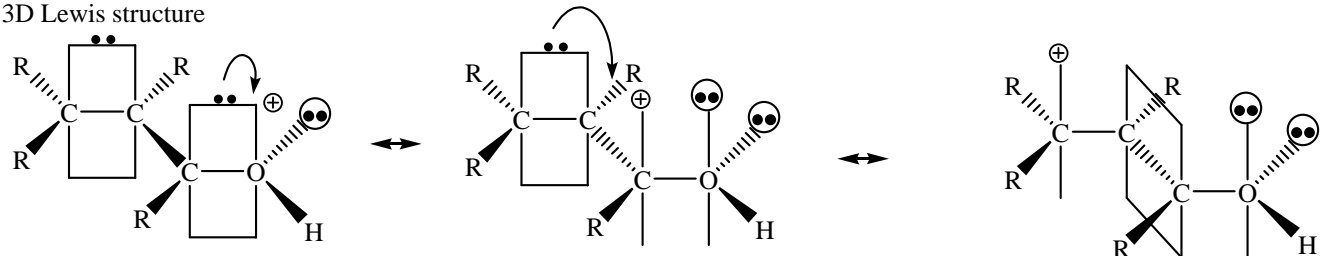


Organic Resonance Systems

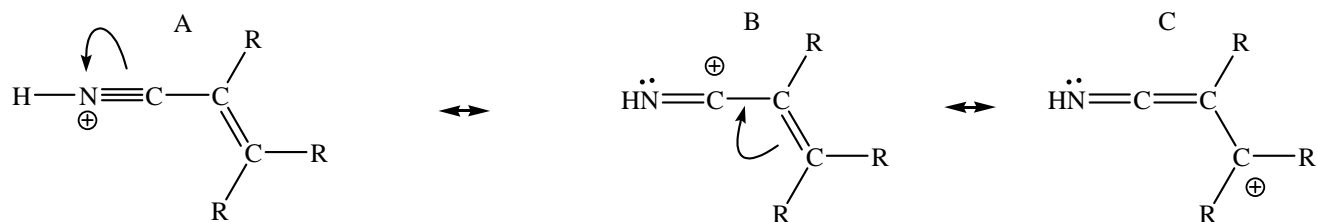
Cationic pi systems: notice the cationic site is spread to multiple centers (three in these examples). Structure A can be shown going directly to C using 2 arrows.



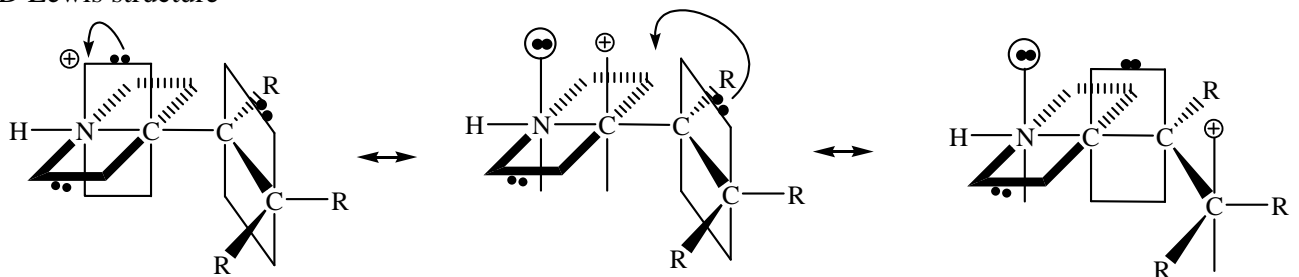
3D Lewis structure



Cationic pi systems: notice the cationic site is spread to multiple centers (three in these examples). Move electrons towards the positive charge. Structure A can be shown going directly to C using 2 arrows.



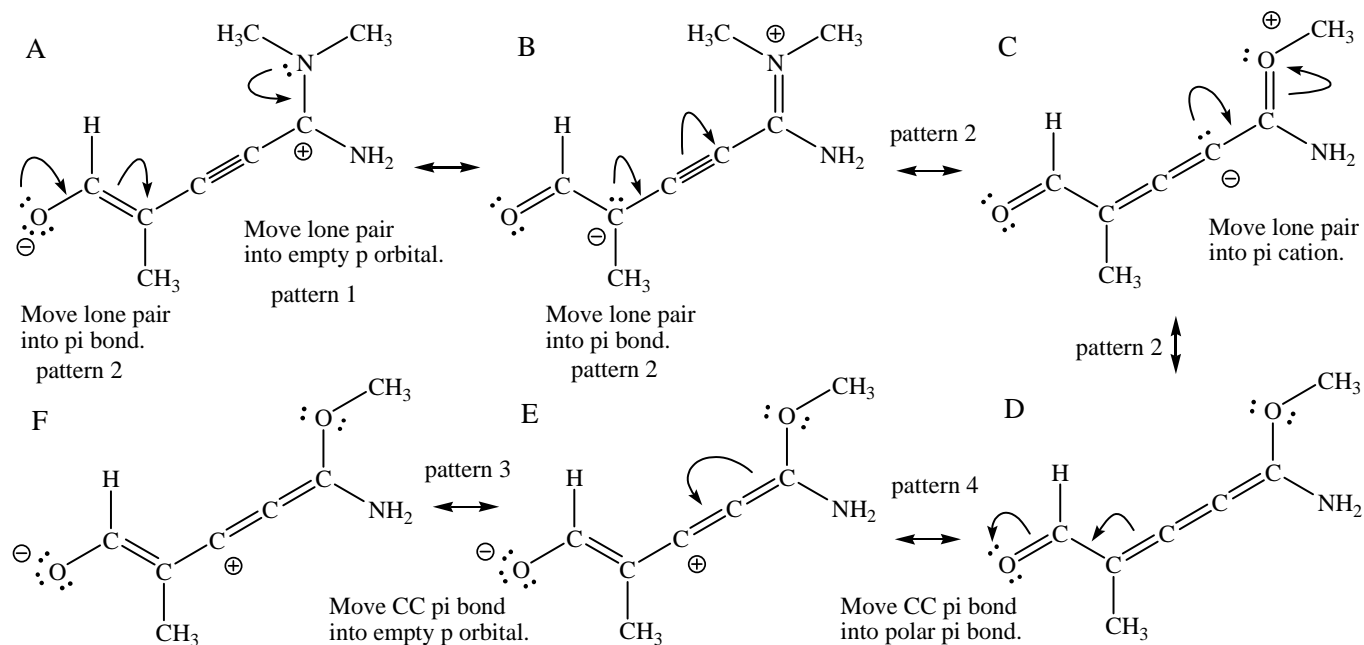
3D Lewis structure



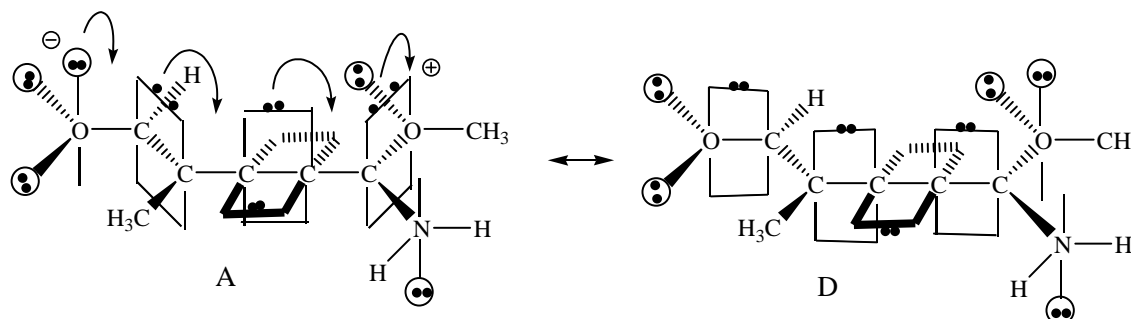
Combination of All 4 Patterns

donor site(s)?
acceptor site(s)?
connector site(s)?

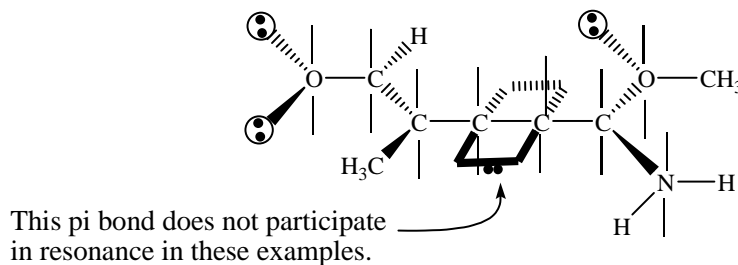
There are other ways to show resonance in these examples beyond what is shown below.



Example of 3D representation (below)

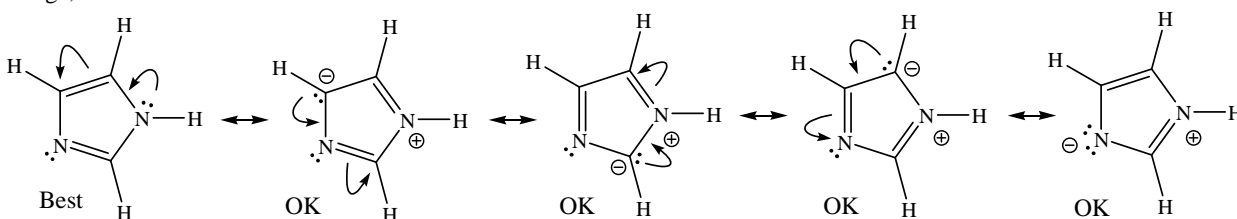


This 3D framework fits all resonance structures above (and more). Delocalization occurs through parallel 2p orbitals.

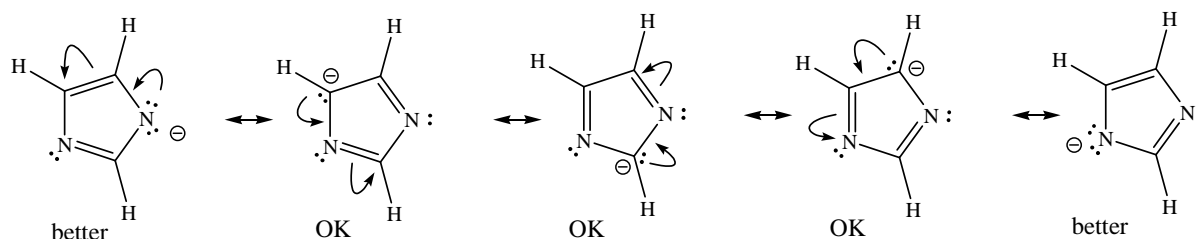


Three variations with resonance in imidazole: neutral, anionic and cationic

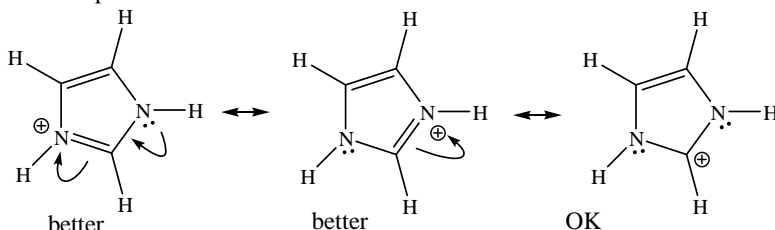
Example 1 - Neutral imidazole: Delocalization of p orbital electrons in a neutral ring structure. Additional structures create charge, but have the same number of bonds and full octets and all are reasonable contributors.



Example 2 - Anionic imidazole: Delocalization of p orbital electrons in an anionic ring structure. The first and last structures are equivalent and the most important contributors because of the greater electronegativity of nitrogen.

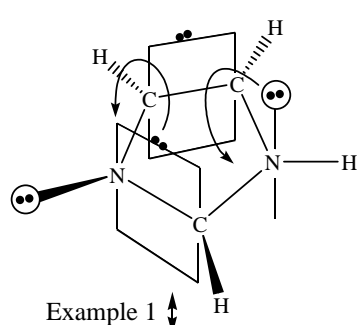


Example 3 - Cationic imidazole: Delocalization of p orbital electrons in a cation ring structure. The first two structures shown are best because they have an extra bond and full octets. One extra structure is shown with positive charge on carbon, but it has an incomplete octet.

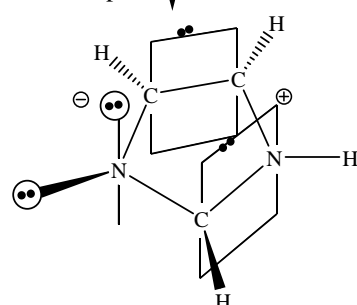


The 3rd structure is not as good as the first two structures. It has fewer bonds and an incomplete octet, but is still a resonance contributor and provides information about the chemical reactivity of this cation.

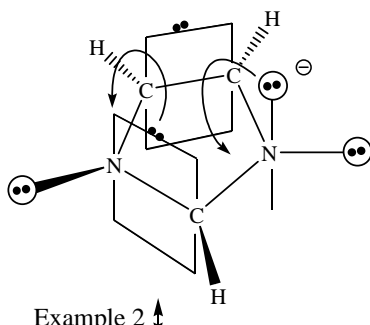
3D template for all resonance structures above. Lone pairs or groups perpendicular to the p orbitals are not part of the resonant system. In some structures the group to the side of the sp^2 nitrogens is a lone pair and in some structures it is a hydrogen atom. In all cases the side group is using an sp^2 orbital. The p orbitals are all part of the resonant system in this problem.



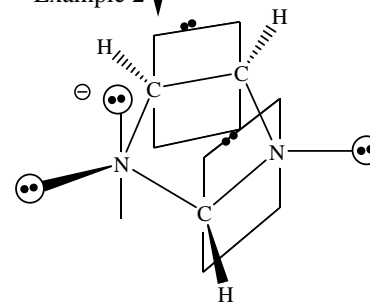
Example 1



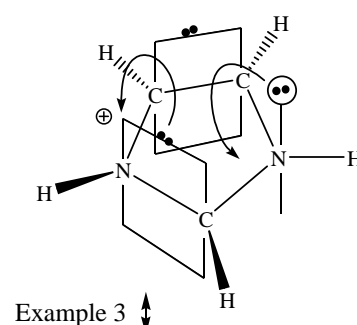
OK resonance, but creates charges in a neutral structure



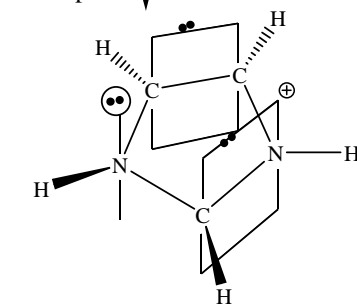
Example 2



Excellent resonance, spreads out high energy negative charge



Example 3



Excellent resonance, spreads out electron density to electron deficient sites.

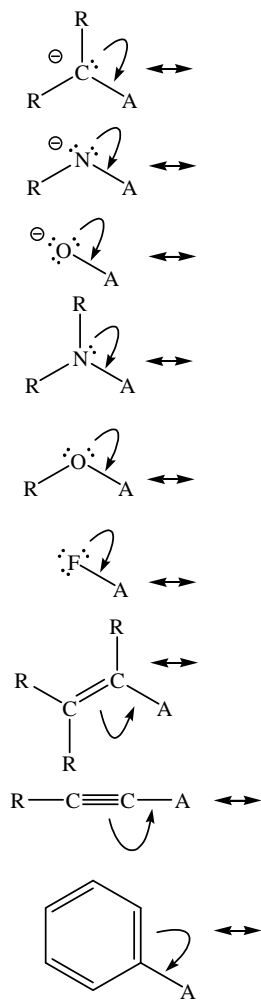
Generic Examples

donors = D
lone pair / pi patterns

lone pairs

- a. neutral (N, O, F)
b. anion (C, N, O)

C/C pi bonds
alkenes, alkynes, aromatics

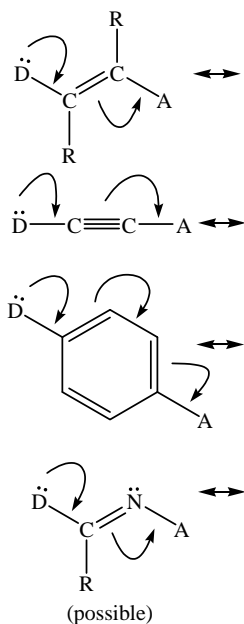


donors = D
acceptors = A

In this slide,

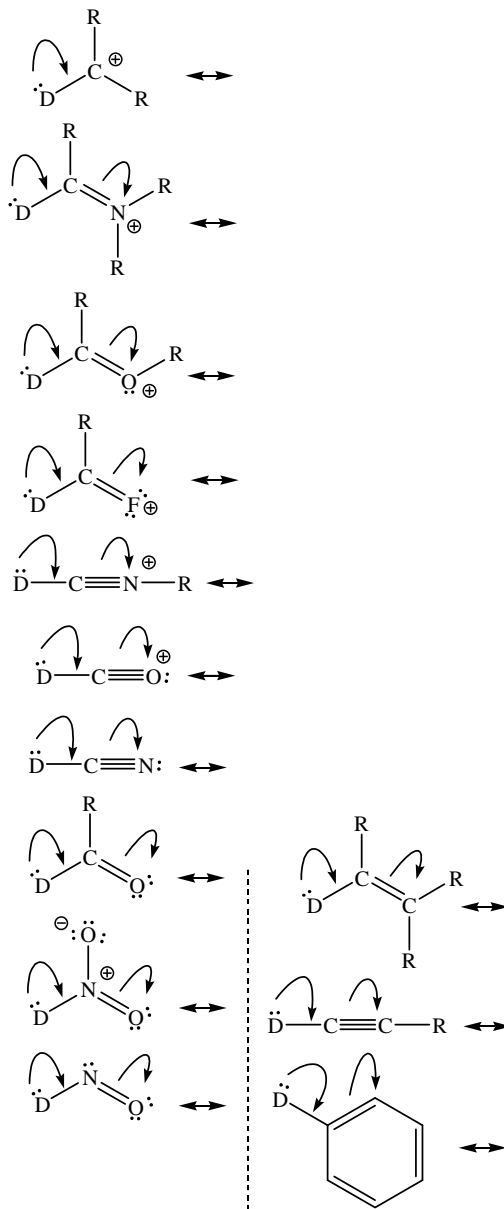
R = C or H
O = S
F = Cl, Br, I

connecting
pi patterns

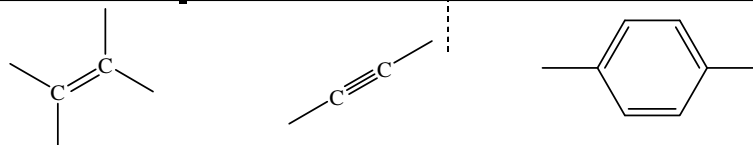


Just a sampling. There are too many variations to show all possibilities.

acceptors = A
empty 2p / pi patterns



connecting pi patterns C/C pi bonds,
usually alkenes, alkynes, aromatics



Possible connector patterns with any combination of the above donors and/or acceptors. The CC pi systems (alkenes, alkynes and aromatics) are similar to a wire that allows electrons to flow throughout. The electron density distributes itself in a manner to optimize the electron-electron repulsion. We call this delocalization or resonance.

