Important reminder about Organic Chemistry

The drawing system is extremely limited because it does not account for delocalization in its symbolism. Recall CH 01: we use an inadequate system of showing localized electron structures and a collection of resonance contributors to convey the idea of electron delocalization. Then we added hyperconjugation as another class of electron delocalization, and now we are adding aromaticity/antiaromaticity (particularly complicating the story because antiaromatic delocalization is unstable).

Electron Delocalization

\( \sigma/p/\pi \): hyperconjugation (as in 3\(^\circ\) carbocation stability > 2\(^\circ\))

\( \pi/\pi \): resonance

The way things worked for assessing resonance delocalization in CH 01:

- Be on the lookout for cases where deloc is not seen (although drawing seems OK)
  - (a) allene or triple bond in small ring
  - (b) \( \geq +2 \) for main group element

Resonance structure of interest

CH 01

Draw (according to general cases) other resonance contributor, evaluate significance

If these were given in CH 01, you would say:

- 4 deloc e
- O atom sp\(^2\)
- (if exists, O sp\(^3\))

- 4 deloc e
- Antiaromatic

- 4 deloc e
- Antiaromatic (highly reactive)

- 4 deloc e
- Aromatic

Assessing for potentially completely cyclic delocalization is an additional criterion for resonance delocalization. It uses its own set of criteria to evaluate the resonance contributor you are examining, and does not begin with the “draw other contributors” strategy.

Resonance structure of interest

CH 10

(a) Is this a ring with sp\(^2\) atoms (p orbitals or the possibility of p orbitals) at every vertex?
  - NO (go back), YES (go on)

(b) Are the p orbitals and pi bonds all endocyclic and have the option to all be parallel (i.e., the ring to be planar? NO (go back), YES (go on)

(c) Count e in p orbitals
  - 4N e

Antiaromatic ring contributor (deloc unstable) adopts loc form, reactive

Aromatic ring contributor (deloc stable) planar, sp\(^2\), low react
Notes: the specific way in which an antiaromatic ring ends up localized or partially localized to avoid the unstable cyclic delocalization is not always predictable. The ring might be large enough to bend and break delocalization. Heteroatoms might adopt localized electron hybridizations (sp\(^3\) rather than sp\(^2\)). Or, barring either of those options, the molecule might just be highly reactive and/or unable to be formed. Among the antiaromatic rings in this set:

(f) reactive, cannot bend, likely lengthens to localize the double bonds as best as possible
(i) large enough to bend, leaving the O atom as OE; LE on the O is another option
(m) both LE likely, as the sp\(^3\) N will start to fold the ring and enable sp\(^3\) at both sides; OE is OK
(s) ring B: isoelectronic with (f), likely lengthens to localize the double bonds
(t) ring B: a highly disfavored contributor compared with the other one in which the two flanking rings are aromatic; the 4-membered ring would likely be stretched to minimize the effect of the delocalization
(a) No

(b) No

(c) No

(d) Yes
(a) There are significantly more resonance contributors for the charge separated form due to resonance stabilization of the benzylic carbocation contributors - and so the dipole moment (based on charge separation) is higher.

(b) The resonance contributor for the cyclopropenone contains an aromatic ring and is a significant contributor to the structure. Given that the dipolar form is highly significant, the dipole moment for the molecule is much larger than for any of the others.

(c) Cyclopropanone has a smaller dipole moment (2.67 D) than acetone (2.91 D), and so the dipolar resonance contributor in cyclopropanone must be relatively less significant to the overall structure.

   (the explanation is likely a difference in how effective the hyperconjugation is in providing stabilization for the dipolar contributor)

(d) the oxygen atom in cyclopropenone is more anionic and so more basic thanks to the aromatic ring, so its conjugate acid will be weaker (-5); alternatively, one can view the conjugate acid as being more stabilized thanks to the aromatic ring, and so that form is more persistent (also the weaker acid with the higher pK\textsubscript{a} value)
favorable resonance stabilization, whereas the other site cannot be delocalized without forming a $\text{O}^{+2}$ contributor.

Protonation of the localized nbe pair does not disrupt the aromaticity of the ring, while protonation at the other site would

Protonation of the localized nbe pair does not disrupt and is stabilized by the delocalized pair from the other N atom; protonation at the other site removes delocalization.

Protonation of the localized nbe pair does not disrupt the aromaticity of the ring, while protonation at the other site would
reacted within seconds  

took an hour  
did not react at all  

is a nonstabilized secondary carbocation  

is a stabilized allylic carbocation  

is a highly nonstabilized antiaromatic carbocation