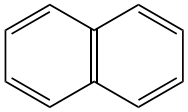
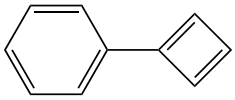
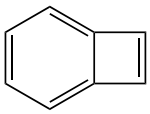
Aromaticity in Molecules with More Than One Ring

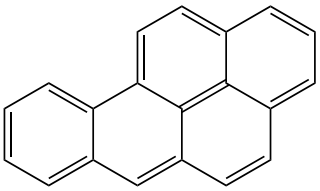
There have been some questions concerning aromaticity in molecules having more than one ring. The following examples are meant to clarify these issues.

Label each of the following molecules as aromatic or not aromatic.

(a) 

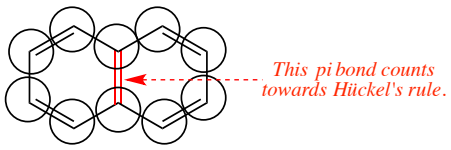
(c) 

(b) 

(d) 

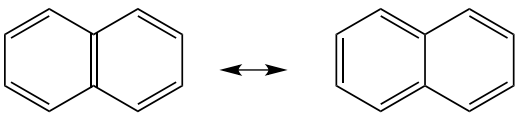
(a) Underlying question: How do I count pi electrons in the bond shared by the two rings? Is this pi bond contained within the closed loop?

Answer: In order to count for Hückel's rule, the orbitals that host the pi electrons in question must all be part of the closed *p* orbital loop. Thus if the electrons in question are a lone pair, the atom hosting the lone pair must be part of the loop. If the electrons under consideration are in a pi bond, both atoms of the pi bond must be part of the closed loop. The bond itself does not have to be between two contiguous closed loop atoms, but instead, can be between any atoms within the loop. So for naphthalene (the molecule in question) the electrons indicated below are counted towards Hückel's rule.



Naphthalene has five C=C (each having two pi electrons) in the closed loop, so this molecule is aromatic.

Here is an alternate (and equally valid) viewpoint. Recall that resonance contributors are alternate representations of exactly the same molecule. We can use any equally valid resonance contributor (that is, a contributor with the same number or less of resonance contributor preference rule violations) to analyze aromaticity. For naphthalene there is another, equally significant resonance contributor:

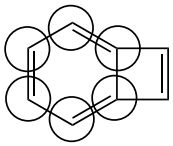


Contributor I Contributor II

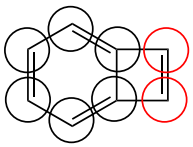
Contributor II is easily seen to have a closed loop of *p* orbitals hosted on a set of coplanar carbon atoms, and to obey Hückel's rule (n=2). Contributor II is aromatic, so naphthalene is aromatic.

(b) Underlying question: Must I include all *p* orbitals in the closed loop, even if counting all predicts the molecule is nonaromatic (or antiaromatic) when counting just some would predict the molecule is aromatic?

Answer: When considering which *p* orbitals to include in the closed loop, we consider only the largest closed loop. We select the loop containing the most *p* orbitals even if this larger loop causes us to conclude the molecule is less stable than if we had used a closed loop using less orbitals or pi electrons. So for the molecule in question:



Selecting this *p* orbital loop is incorrect because additional *p* orbitals can be included. Selecting this loop may lead you to conclude this molecule is aromatic (because the loop hosts six pi electrons) but this is a false conclusion because it is based on a false loop selection.

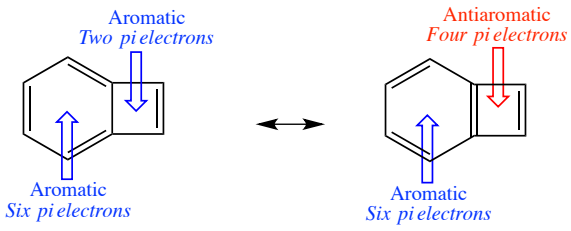


This is the correct *p* orbital loop selection because it includes the greatest number of *p* orbitals within the loop. This loop hosts eight pi electrons, making the molecule antiaromatic. You may have chosen to skip or ignore the *p* orbitals circled in red because the loop in black has six pi electrons, but (because it ignores some *p* orbitals) this would be an incorrect approach.

(c) Underlying question: If part of a molecule is aromatic but another part is nonaromatic or antiaromatic, is the whole molecule aromatic, or what?

Answer: There are two common cases in which this question might arise.

Case 1: Fused rings. Rings are said to be fused when they share a side. Benzocyclobutadiene, the molecule in part (b) above, is fused. If we treat the fused rings separately, we might conclude the benzene ring portion (with its six pi electrons) is aromatic, and the cyclobutadiene ring portion is also aromatic (with its two pi electrons). Or based on what we learned in part (a) above, we might draw resonance contributor IV, and from this conclude the benzene ring portion (with its six pi electrons) is aromatic but the cyclobutadiene ring (with its four pi electrons) is antiaromatic.



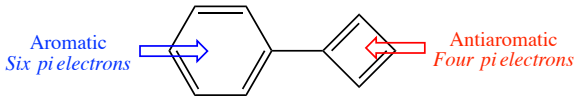
Contributor III Contributor IV

So which is interpretation/prediction correct?

The answer is that neither of these interpretations is correct, because we failed to consider the largest *p*-orbital loop. The correct answer is that we consider the fused

rings together, note that the molecule has eight pi electrons within the closed loop, and conclude (correctly) that the molecule is antiaromatic. Review the answer to part (b) above if you've forgotten how to treat fused ring cases.

Case 2: More than one ring but the rings are not fused. In this case the benzene ring is aromatic and the cyclobutadiene ring is antiaromatic. The molecule has resonance (draw one more significant contributor), but this resonance doesn't change the answer.



So is this molecule aromatic or antiaromatic, or neither, or both, or what?

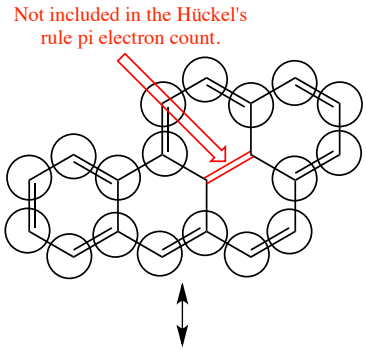
As a whole, the molecule is not aromatic or antiaromatic. It has an aromatic portion and an antiaromatic portion but neither term fully describes the molecule. The aromatic and antiaromatic parts do not cancel out. So for this molecule the correct label is "it has an aromatic part and an antiaromatic part".

A metaphor: If your car is half blue and half yellow, is the car's color fully described by calling it blue, or by calling it yellow? No it is not. So we label it as blue *and* yellow.

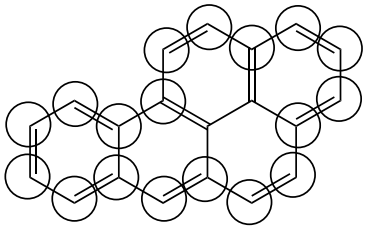
So for the molecule shown above, we could say that is has both aromatic and antiaromatic portions or properties.

(d) Underlying question: How do I determine the *p* orbital loop and pi electron count when some of the *p* orbitals lie inside the loop?

Answer: For this point the given molecule is benzo[a]pyrene, a human carcinogen found in tobacco smoke, e-cig vapor, asphalt, tar, petroleum, burnt meat, and some other places. Data from laboratory experiments tells us that benzo[a]pyrene has all of the characteristics of an aromatic compound, such as high stability and planarity, even though its adherence to Hückel's rule is uncertain. To see this, circle the *p* orbital loop atoms of benzo[a]pyrene, then count the number of pi electrons in this loop:



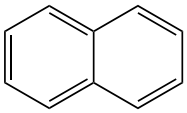
Here the *p*-orbital loop encompasses nine C=C, each providing two pi electrons. (The central C=C isn't hosted by the largest *p* orbital loop, so it's not counted towards Hückel's rule.) The total pi electron count is 18, which is a 4n+2 number (n=4). So this resonance contributor suggests benzo[a]pyrene is aromatic.



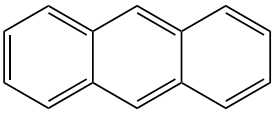
In this benzo[a]pyrene resonance contributor, eight C=C contribute a total of 16 pi electrons. The two C=C whose carbons are not both part of the loop cannot be counted. Sixteen pi electrons is not a 4n+2 number. This resonance contributor is antiaromatic.

A few additional resonance contributors that can be drawn, some aromatic and some not, add to the confusion. So what is the correct interpretation or prediction?

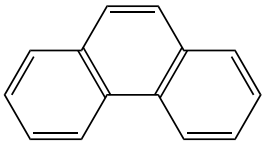
In general, molecules with two or more fused benzene rings (and nothing else to change the pi electron count, such as rings other than benzene, or lone pairs) are aromatic, regardless of the Hückel's rule pi electron count. This is because the simplistic closed loop/Hückel's rule analysis for aromaticity can fail in some of these cases. Based on laboratory data, the following molecules are all aromatic:



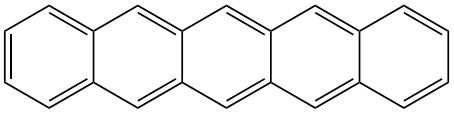
Naphthalene



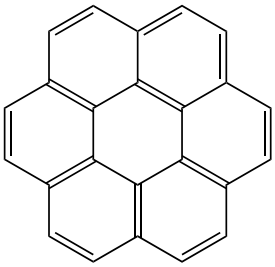
Anthracene



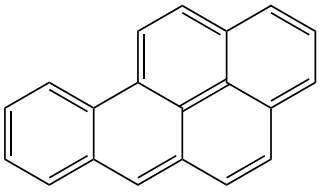
Phenanthrene



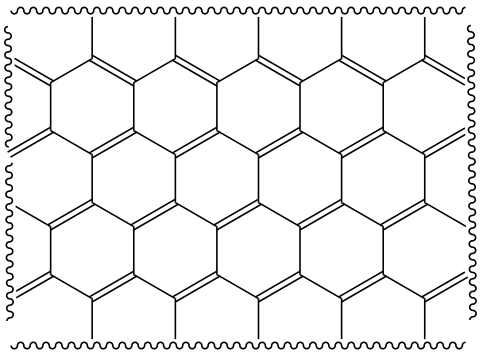
Pentacene



Coronene



Benzo[a]pyrene



Graphene

Essentially an infinite sheet of fused benzene rings.

So when you see fused benzene rings (and nothing else to disturb the pi electron count), label the molecule as aromatic.