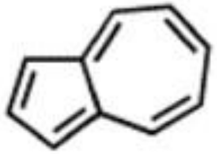
What does 4n+2 mean?

“n” is not a characteristic of the molecule!



In order for a molecule to be aromatic, it has to have the following characteristics:

It must be cyclic
It must be conjugated (i.e. all atoms around the ring must be able to participate in π-bonding through resonance)
It must be flat
And, it must have a certain number of π-electrons. This is known as Huckel’s rule. The number of π electrons must equal one of the numbers in this series:
2, 6, 10, 14, 18….and so on. For example, we can find aromatic molecules with 2 pi electrons, 6 pi electrons, 10 pi electrons, 14 pi electrons, 18 pi electrons, and so on. But we have never found aromatic molecules with 0, 1, 3, 4, 5, 7, 9, 11, 12, 13, 15, 16, 17 (and so on) pi electrons. Those numbers are not in the series.
To reprise: the number of pi electrons in an aromatic molecule will always be found in the series [2, 6, 10, 14, 18 …and so on]
However, there has to be a better way of expressing it than [2, 6, 10, 14, 18… and so on”]

Let’s plug in different values of n (we will put n in bold)
For the formula $4n + 2$
For $n = 0$, we get $(4 \times 0 + 2) = 2$
For $n = 1$, we get $(4 \times 1 + 2) = 6$
For $n = 2$, we get $(4 \times 2 + 2) = 10$
For $n = 3$, we get $(4 \times 3 + 2) = 14$
For $n = 4$, we get $(4 \times 4 + 2) = 18$
We can keep going, but do you get the idea?
By using the formula [4n +2], we are expressing the same idea as [2, 6, 10, 14, 18… and so on] but it is a lot more precise.

So “n” comes from algebra, NOT from chemistry.

Molecules that have the 3 characteristics listed above (cyclic, conjugated, flat) and have this number of π electrons [4n +2] will be aromatic. The letter “n” is not a characteristic of the molecule!

2 π electrons

Aromatic

4 π electrons

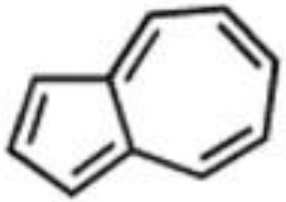
Not Aromatic

6 π electrons

Aromatic

8 π electrons

Not Aromatic



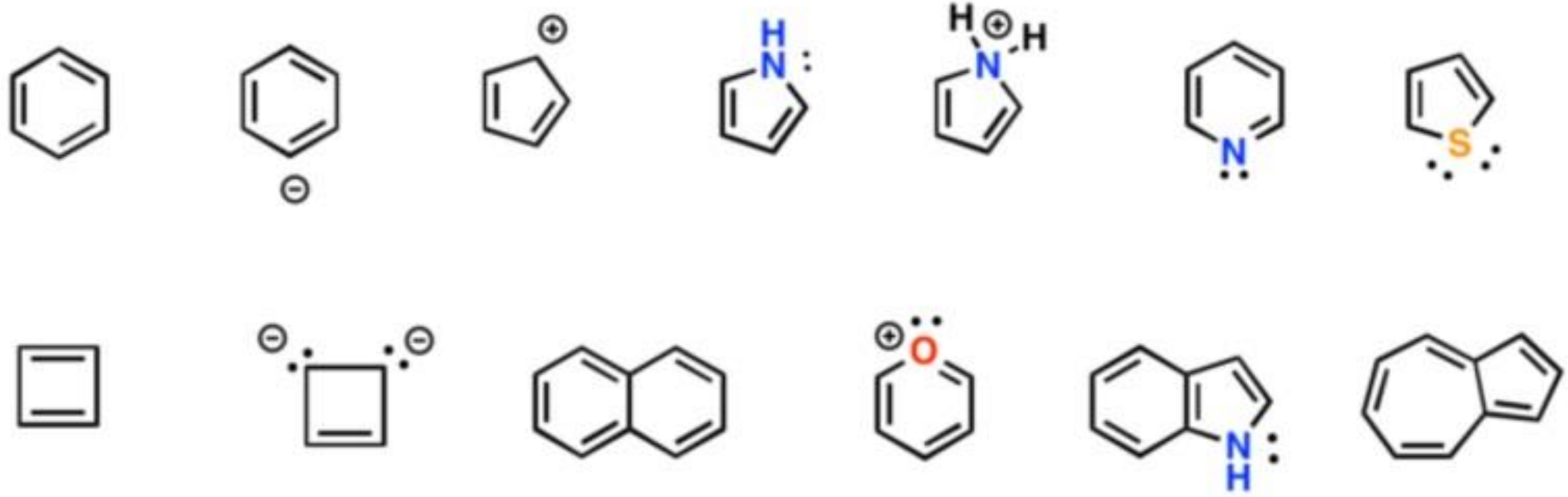
10 π electrons

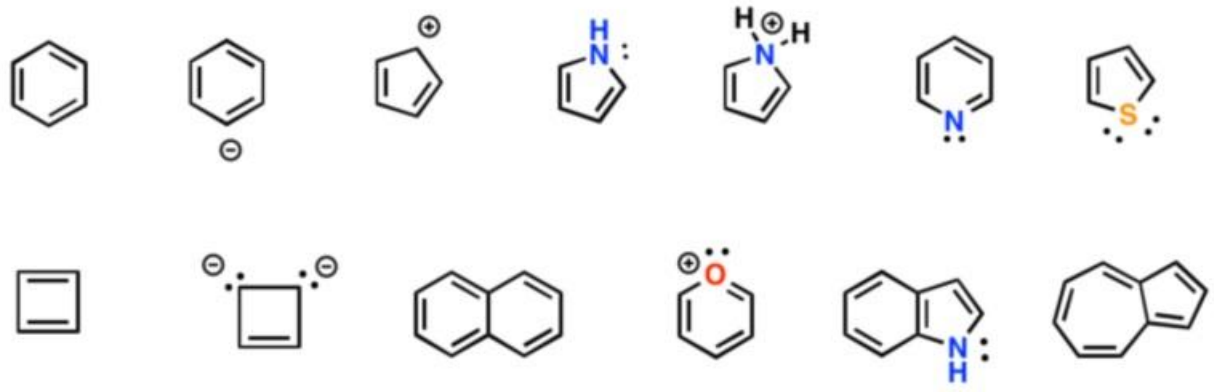
Aromatic

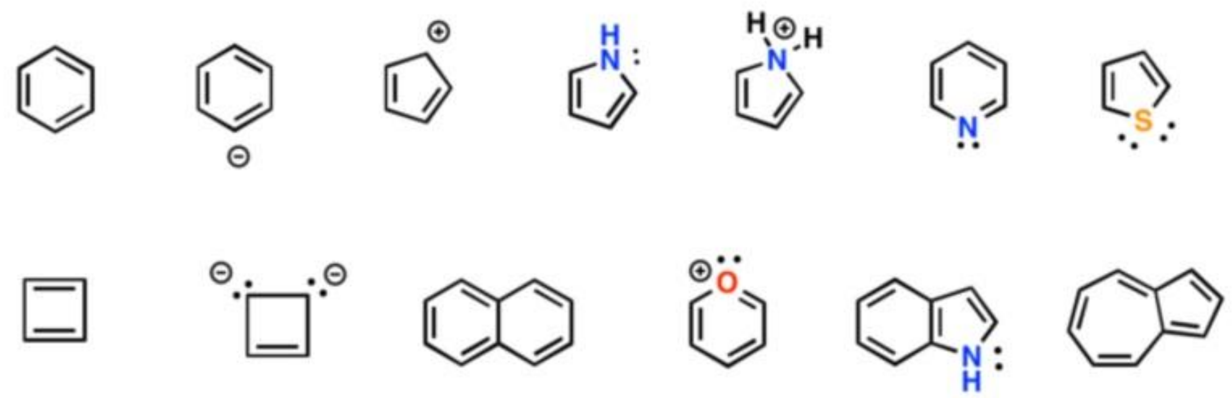
Is This Molecule Aromatic?

- It must be cyclic
- Every atom around the ring must have an available p-orbital
- The number of electrons in the pi system must be 2, 6, 10, 14, 18, or a higher number in the set that increases from 18 in increments of 4 (22, 26, 30…. etc). We usually abbreviate this as [4n+2] pi electrons.
- The molecule must be flat.

Which molecule is Aromatic?



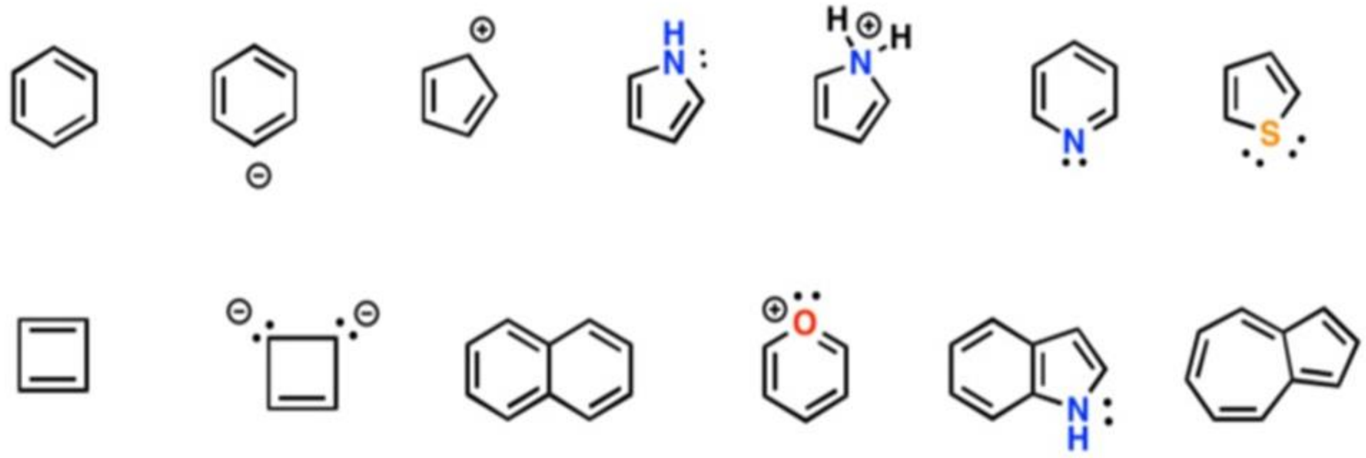




Benzene

The easiest example to start with is benzene, and it demonstrates how to use the table. It's cyclic, conjugated, has 3 pi bonds and those pi bonds are all in the pi system. It has zero lone pairs that contribute to aromaticity. Therefore it has (3 × 2) + 0 = 6 pi electrons. We're assuming it's flat (it is). Checking off all the boxes, we can say that it's aromatic.

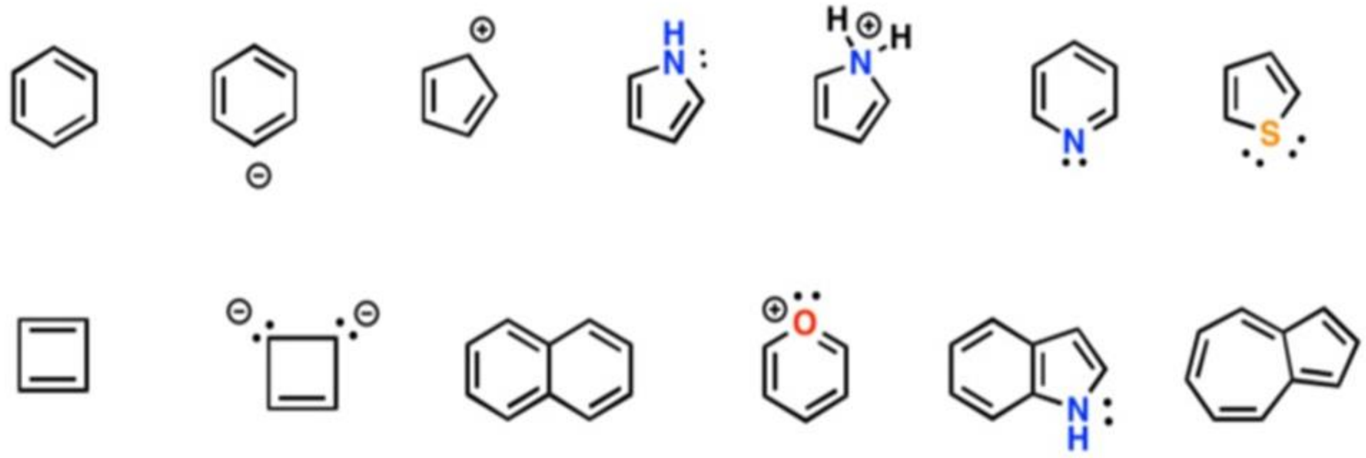
Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Benzene	Y	Y	3	0	6	Y	?



The benzene anion

If you remove a proton from benzene, you get the benzene anion. Like benzene, it's cyclic, conjugated, had 3 pi bonds and those pi bonds are all in the pi system. It's tempting to look at that lone pair and to think that it might contribute to the pi system as well, giving 8 pi electrons total. However, that lone pair is in the plane of the molecule (along with the other C-H bonds) and thus can't overlap with the p-orbitals. Therefore, for the purposes of determining aromaticity, we can ignore the lone pair.

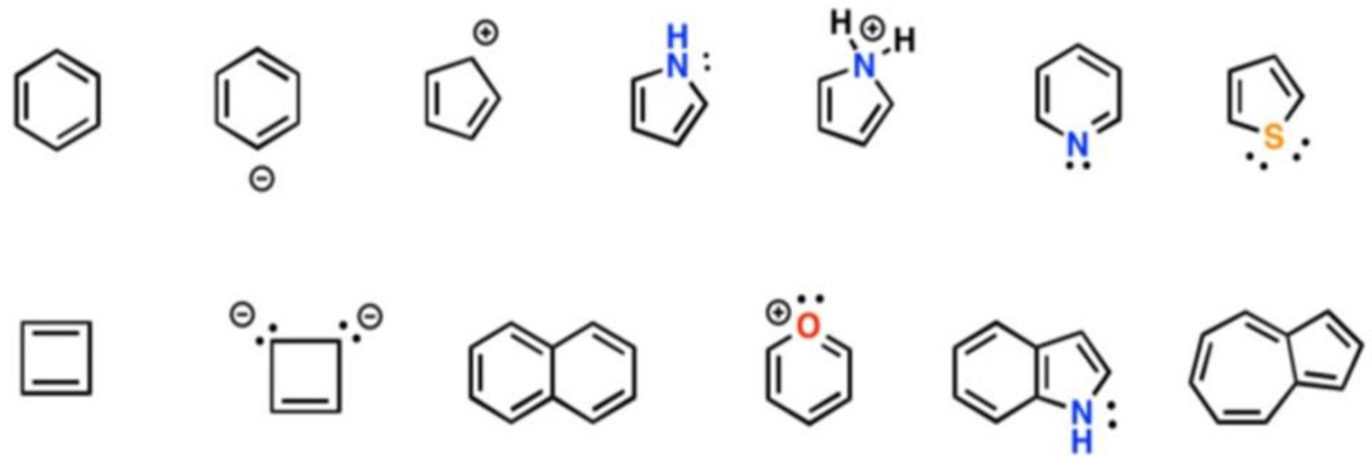
Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Benzene anion	Y	Y	3	0	6	Y	?



The cyclopentadiene cation

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
cyclopentadiene cation	Y	Y	2	0	4	N	?

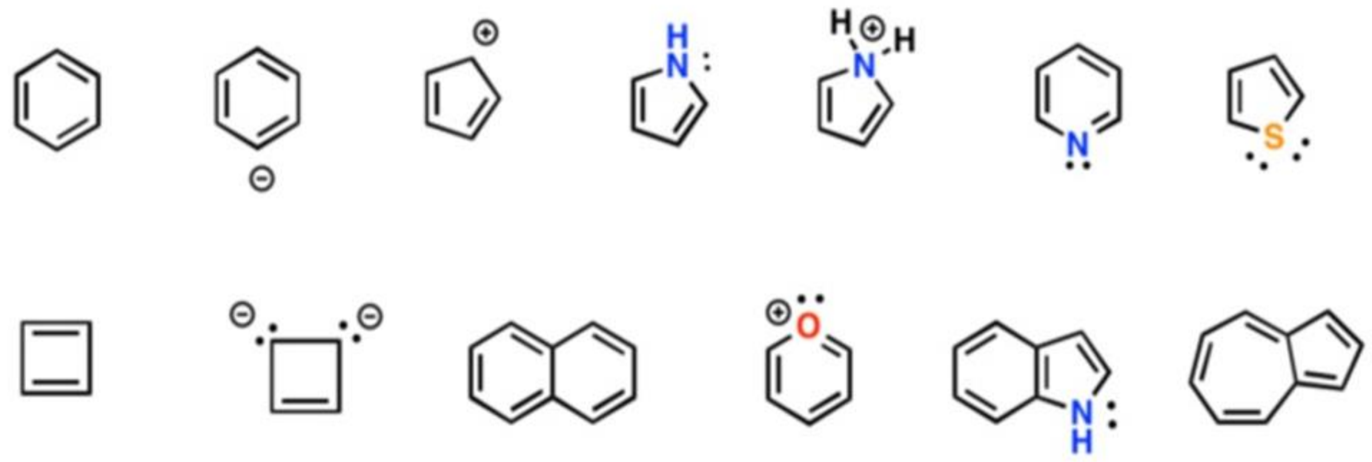
The cyclopentadiene cation below is cyclic and conjugated (that positive charge represents a carbocation with an empty p-orbital). There are two pi bonds and zero lone pairs to contribute to the pi system. This gives us 4 total pi electrons, which is not a Hückel number. Therefore it isn't aromatic.



Pyrrole

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Pyrole	Y	Y	2	2	6	Y	?

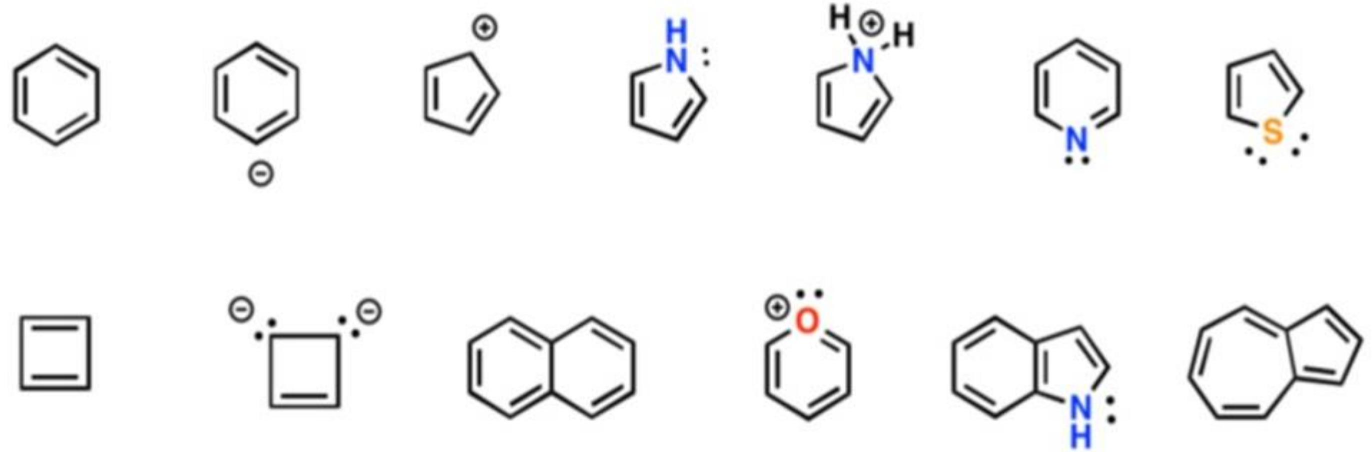
Pyrrole is cyclic and conjugated (that lone pair on nitrogen can contribute to the pi-system). There are two pi bonds and one lone pair of electrons that contribute to the pi system. This gives us 6 total pi electrons, which is a Huckel number (i.e. satisfies 4n+2). Therefore it’s aromatic.



Pyrrole Conjugate Acid

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Pyrole conjugate acid	Y	N					?

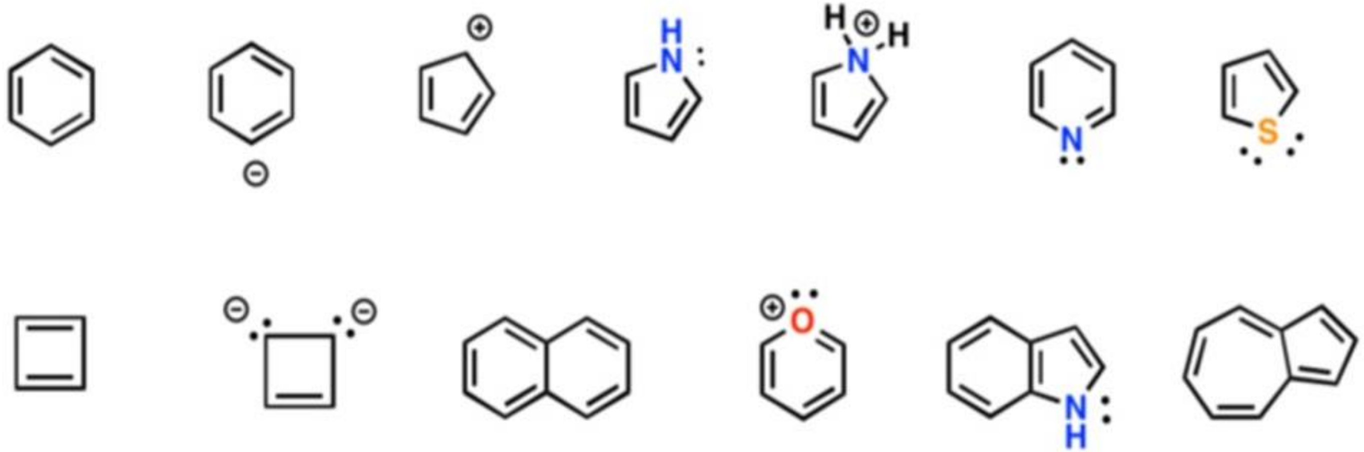
If pyrrole is protonated on the nitrogen, the lone pair can no longer participate in the pi-system. Therefore the molecule drawn below is not aromatic.



Pyridine

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Pyridine	Y	Y	3	0	6	Y	?

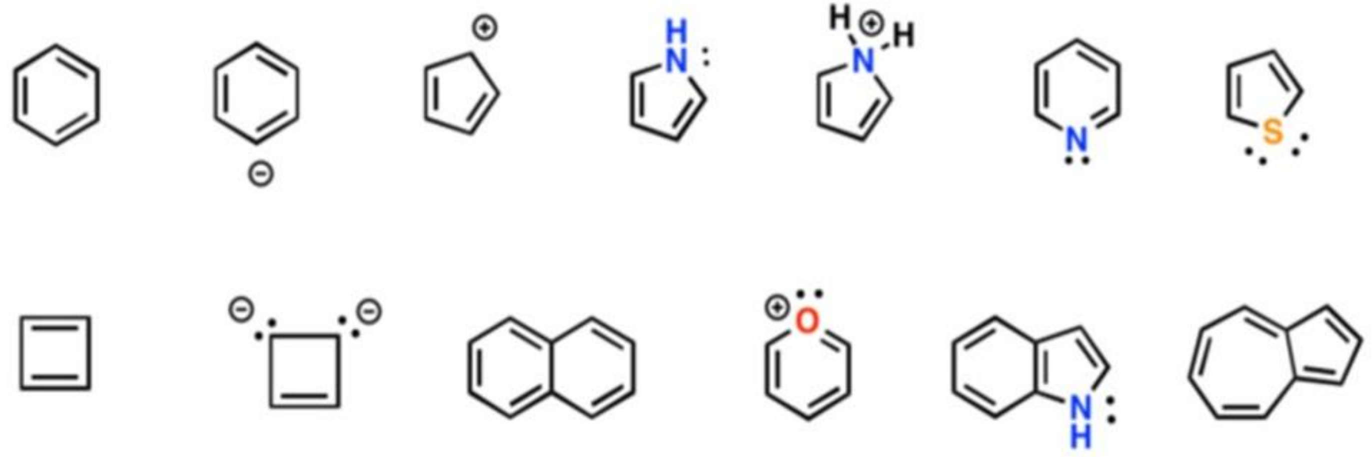
Pyridine is cyclic, conjugated, and has three pi bonds. It's a lot like the benzene anion in that the lone pair looks like it might contribute to the pi system, but in fact is in the plane of the ring (along with the C-H bonds) and thus cannot contribute (the nitrogen is already contributing a p-orbital towards the pi-system – note that it's drawn as participating in a double bond with an adjacent carbon). Therefore we can ignore the lone pair for the purposes of aromaticity and there is a total of six pi electrons, which is a Huckel number and the molecule is aromatic.



Thiophene

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Thiophene	Y	Y	2	2	6	Y	?

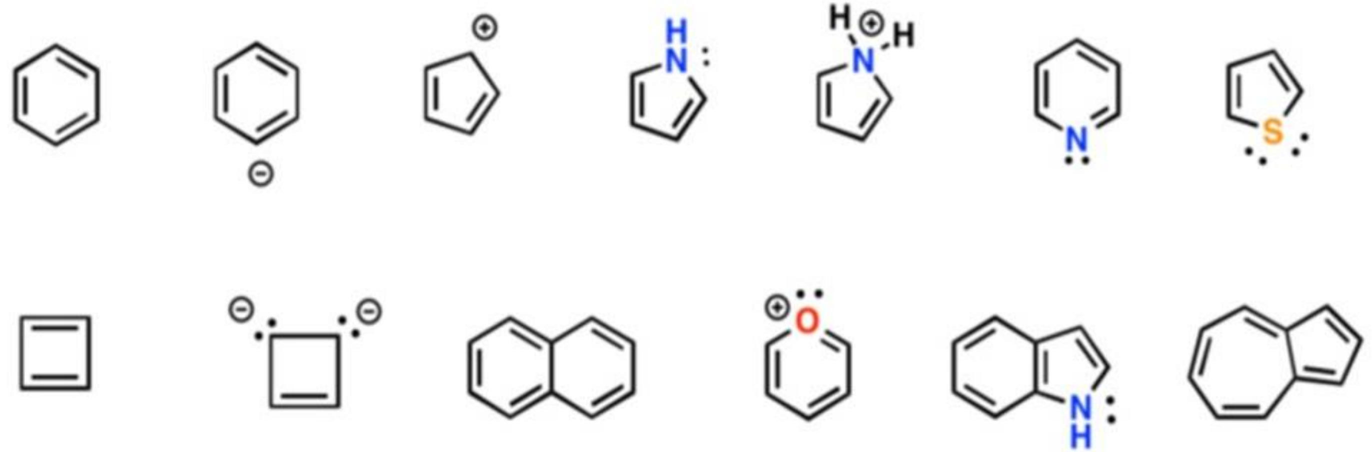
Thiophene, the sulfur analog of furan, is cyclic and conjugated all the way around the ring. It has two pi bonds. What's interesting about thiophene (and furan) is that although there is an atom bearing two lone pairs in the ring, we can only count one of those lone pairs toward the pi-system. [Each atom can contribute a maximum of one orbital and two electrons towards aromaticity]. The other lone pair is in the plane of the ring, much like the lone pair on the nitrogen of pyridine, above. Therefore thiophene has six pi electrons total, which is a Huckel number, and thiophene is aromatic.



Cyclobutadiene

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Cyclobutadiene	Y	Y	2	0	4	N	?

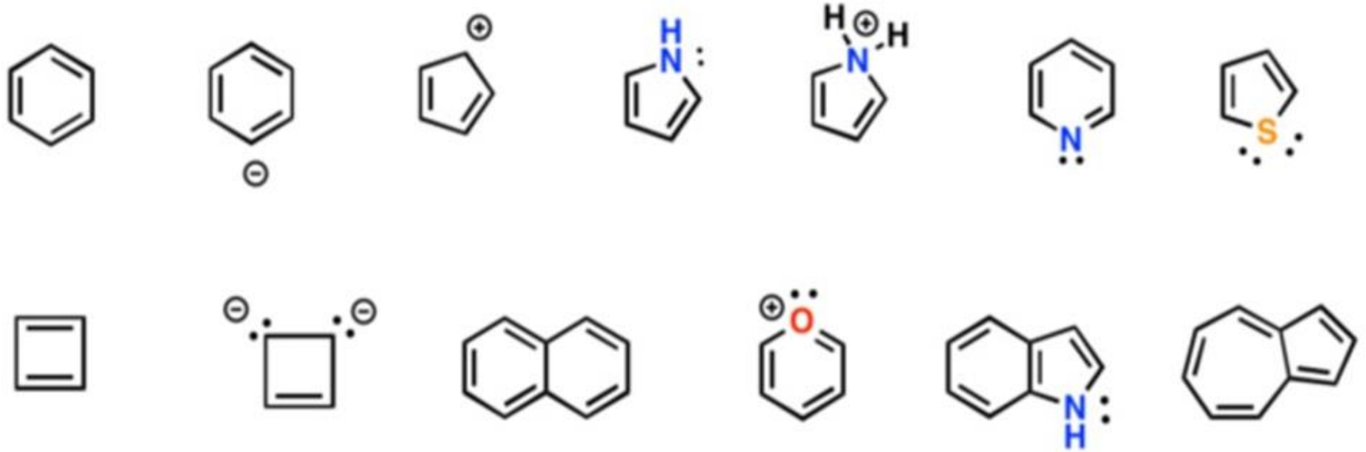
Cyclobutadiene is cyclic and conjugated. There are two pi bonds and zero contributing lone pairs. Two pi bonds gives us a total of 4 pi electrons, which is not a Huckel number. Therefore it is not aromatic, just like the cyclopentadienyl cation, above.



Cyclobutene Di-Anion

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Cyclobutadiene dianion	Y	Y	1	4	6	Y	?

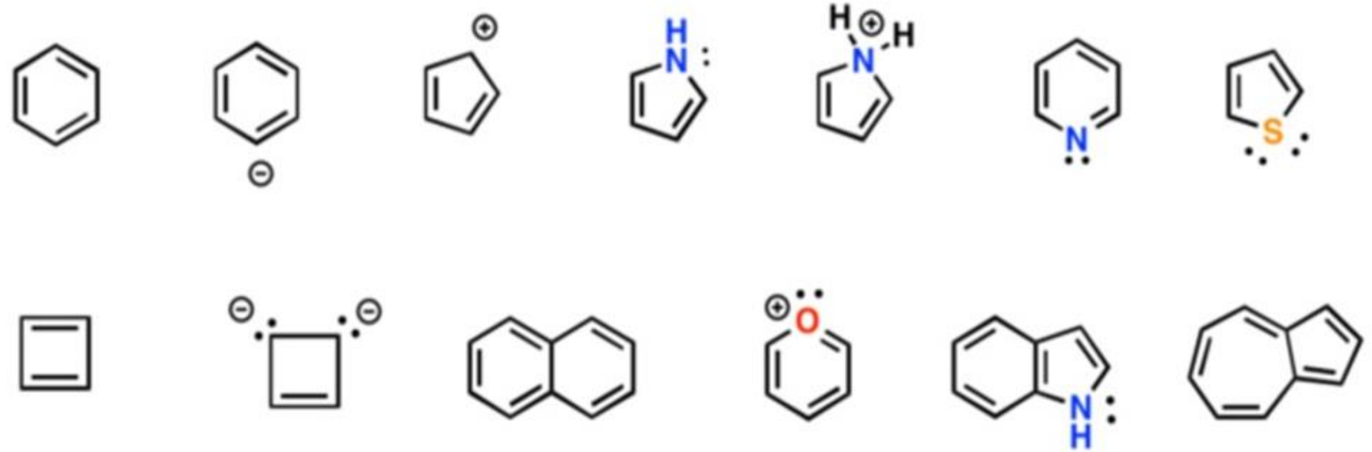
Cyclobutadiene is not aromatic. If we somehow pump two electrons into cyclobutadiene, however, then the situation changes considerably. The cyclobutadiene dianion is cyclic and conjugated. It has a single pi bond, and now two carbons bearing lone pairs which can contribute to the pi system, giving us a total of six pi electrons. This is a Huckel number and thus the cyclobutadiene di-anion is aromatic!



Naphthalene

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Naphthalene	Y	Y	5	0	10	Y	?

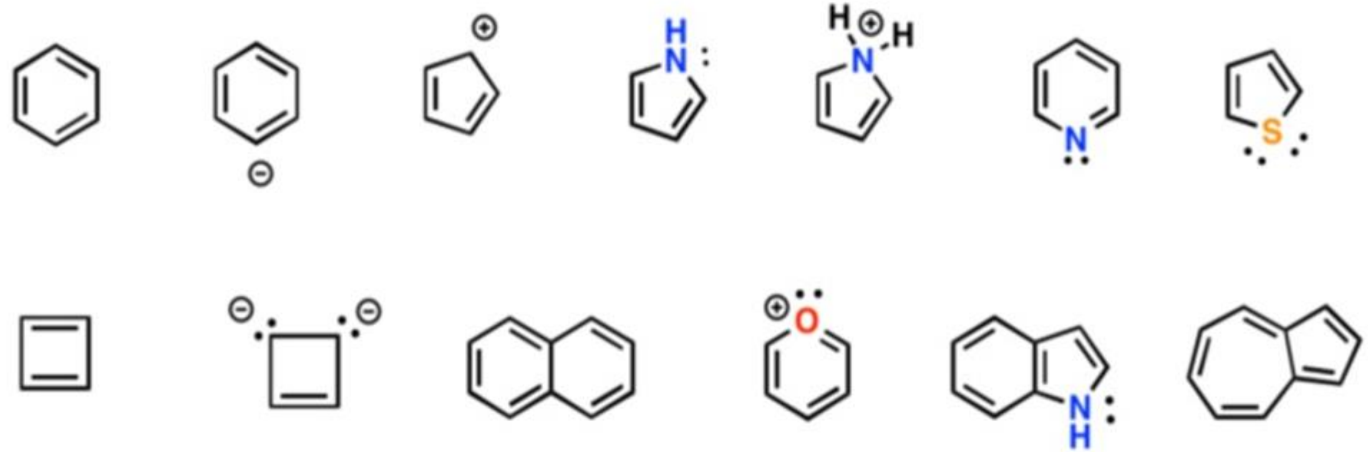
Naphthalene has two rings and is thus a bicyclic compound. It is conjugated around the perimeter of the rings and there are a total of 5 pi bonds and zero lone pairs, giving us 10 pi electrons total. 10 is a Huckel number (satisfying 4n+2 for n=2) and naphthalene is an aromatic molecule.



Pyrylium Ion

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Pyrylium Ion	Y	Y	3	0	6	Y	?

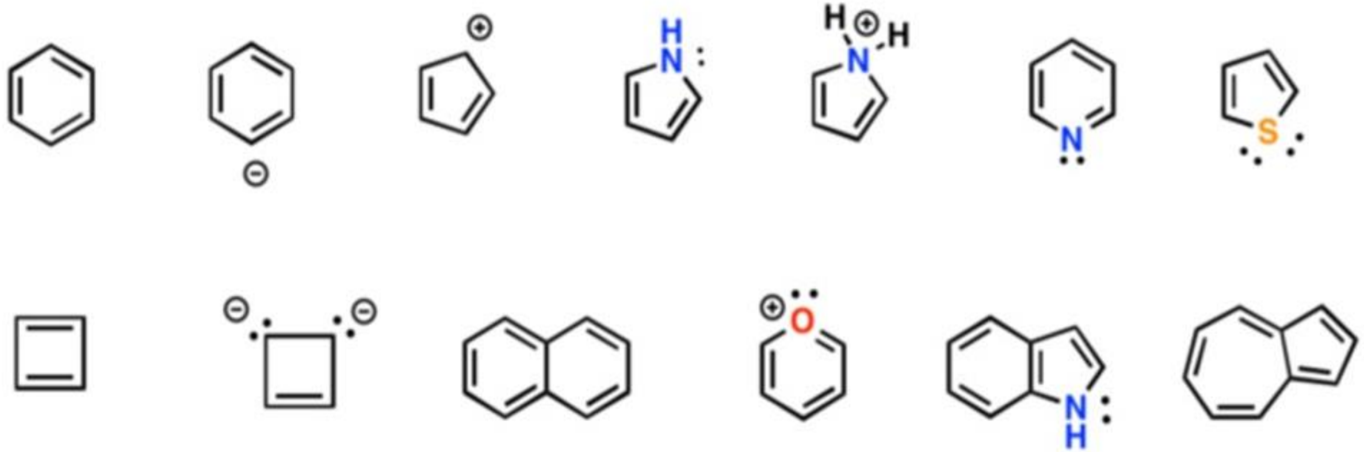
The pyrylium ion is a six-membered ring that, like benzene, has three pi bonds. It also bears a lone pair on the oxygen. Like pyridine and the benzene anion, this lone pair is actually in an orbital at right angles to the pi system so it does not in fact count towards aromaticity. Therefore the molecule has only 6 electrons in the pi system and is in fact aromatic.



Indole

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Indole	Y	Y	4	2	10	Y	?

Indole is a bicylic molecule that looks like a molecule of benzene fused to a molecule of pyrrole. It is conjugated; every atom around the perimeter of the two rings participates in the pi system. It has 4 pi bonds and a single pair of electrons on the nitrogen that participates in the pi system, giving 10 pi electrons in total. This is a Huckel number and indole is in fact aromatic.

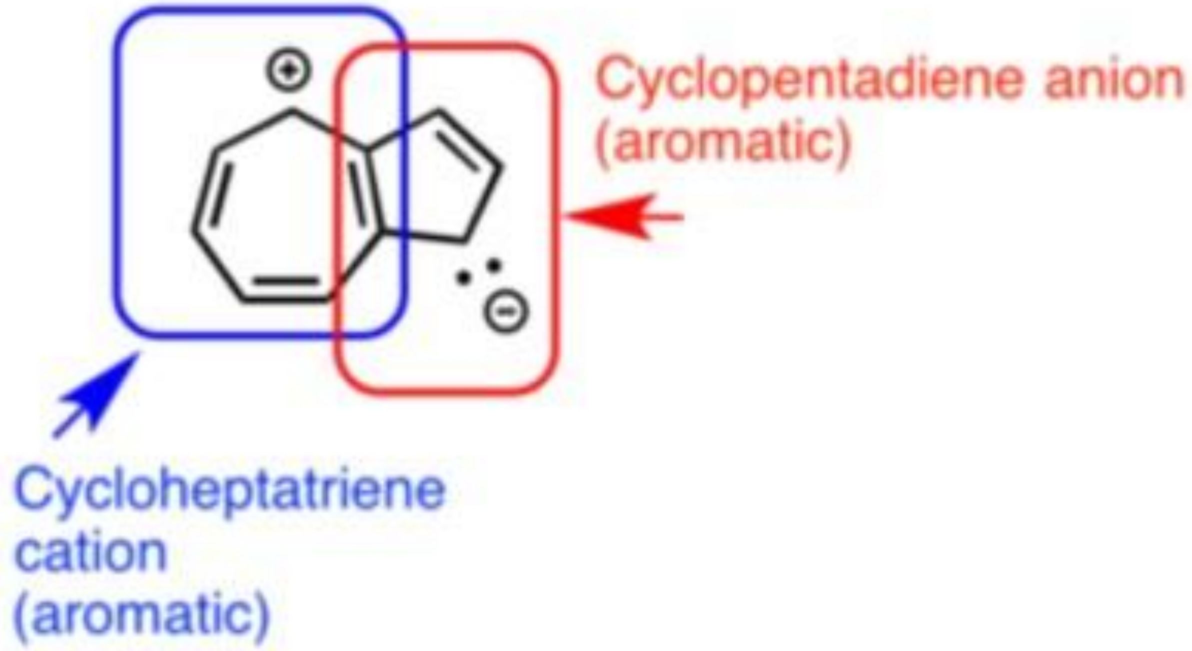


Azulene

Molecule	Cyclic	Conjugated	Pi Bonds	Lone pair pi electrons	Total Pi electrons	4n+2	Aromatic
Azulene	Y	Y	5	0	10	Y	?

Azulene is another example of a bicyclic molecule, like naphthalene and indole, above. It's conjugated all around the perimeter of the pi system. There are five total pi bonds and zero lone pair electrons, giving a total of 10 pi electrons, which is a Huckel number. And azulene is, in fact, aromatic.

If it’s hard to visualize azulene as aromatic, it might be helpful to draw a resonance form where both rings look like they have aromatic components. For example, in the resonance form below, you can think of azulene as being composed of the cycloheptatriene cation (aromatic) fused to the cyclopentadiene cation (also aromatic).



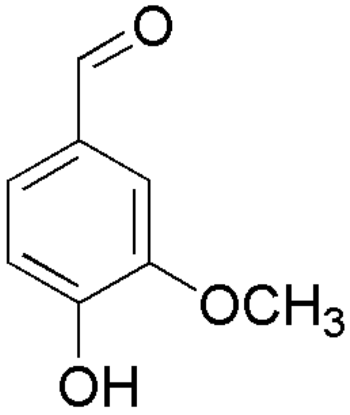
Note that one ring bears a negative charge and the other one bears a positive charge. It turns out that this resonance form has a significant contribution to the hybrid, since azulene itself has a substantial dipole moment (1.08 D). Naphthalene, in contrast, completely lacks a dipole moment.

Rules For Aromaticity

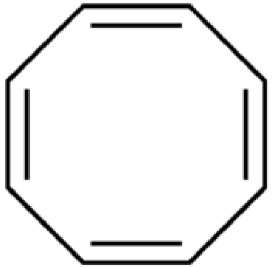
Although some aromatic molecules are indeed fragrant (vanillin) the term “aromaticity” actually has nothing to do with smell.

We saw that aromatic molecules:

- Have an extremely high resonance energy (36 kcal/mol for benzene)
- Undergo substitution rather than addition reactions
- Have delocalized pi-electrons



Given a few example of other molecules besides benzene which are aromatic, and some which look similar to benzene (e.g. cyclooctatetraene) which are not.



cyclic

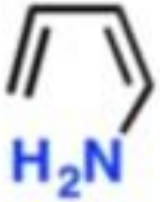
Benzene
Aromatic

acyclic

(Z)-1,3,5 hexatriene
Not aromatic

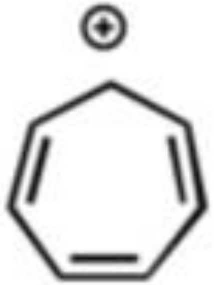
cyclic

Pyrrole
Aromatic



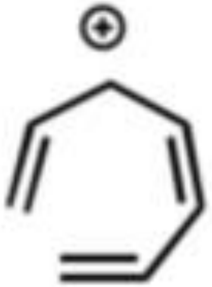
acyclic

Not aromatic



cyclic

"Tropylium" ion
Aromatic



acyclic

Not aromatic

Just to be clear: not all cyclic molecules are aromatic...

cyclohexene
(not aromatic)

tetrahydrofuran
(not aromatic)

The molecule must be cyclic,

Every atom in the ring must be conjugated

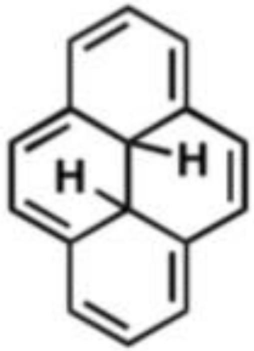
Being cyclic isn't a sufficient condition for aromaticity. Just look at cyclohexene, above right. Not aromatic. In order for aromaticty to exist, there must also be a continuous ring of p-orbitals around the ring that build up into a larger cyclic "pi system".

- Every atom in the ring must have an available p orbital,
- Every atom in the ring must be able to participate in resonance.

The Molecule Must Have [4n+2] Pi Electrons

The Molecule Must Be Flat

A strange case of aromaticity



Interior 2 carbons are sp^3 hybridized

Aromatic!

10 pi electrons, cyclic, ring carbons conjugated, flat.

It should be noted that Huckel’s rule starts to break down for higher numbers of pi electrons (>20) in polycyclic systems.

Hückel's rule is not valid for many compounds containing more than three fused aromatic nuclei in a cyclic fashion. For example, pyrene contains 16 conjugated electrons (8 bonds), and coronene contains 24 conjugated electrons (12 bonds). Both of these polycyclic molecules are aromatic, even though they fail the 4n + 2 rule. Indeed, Hückel's rule can only be theoretically justified for monocyclic systems.