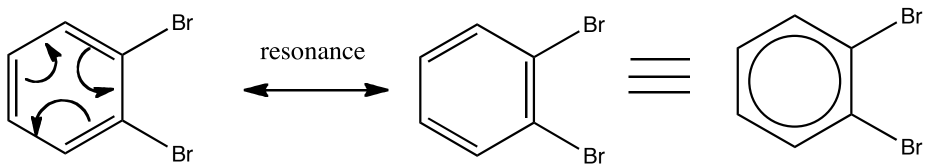
Aromatic Compounds Continued

Aromaticity

Equivalent resonance forms gives stability to a compound.



1,2-dibromobenzene

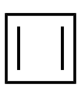
Aromatic compounds are especially stable. For benzene, the delocalization energy (stability) is 36 kcal/mol relative to that expected for cyclohexatriene.

To be **aromatic** (have aromaticity):

1. The molecule is *cyclic*.
2. The molecule is *fully conjugated*.
3. The molecule is *planar*.
4. The molecule contains *4n+2 π electrons*, where n = 0, 1, 2, 3 …

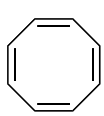
Benzene fulfills all the above criteria. It is conjugated (has three pairs of alternating double and single bonds), it is cyclic and planar, and it has 6 π electrons (where n = 1).

Cyclobutadiene



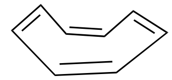
This molecule is cyclic, apparently fully conjugated, and planar.
How many π electrons does it have?
Answer: 4
Is this molecule aromatic?
Answer: No. It does not fit the 4n+2 rule.

Cyclooctatetraene

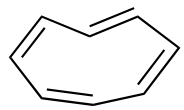


Is this molecule aromatic?
Answer: No. It has 8 π electrons, so it does not fit with 4n+2 rule

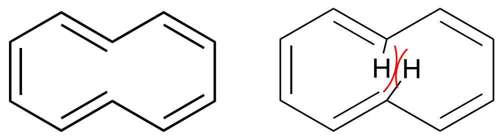
In addition, cyclooctatetraene does not adopt a planar conformation. It is actually tub-shaped. In planar cyclooctatetraene, there is some angle and torsional strain. The angle in regular flat octagon is 135°, far from the optimum sp^2 value of 120°, hence the tub shape.



cis-trans isomerization does not occur in this molecule, and the trans isomer shown below does not exist because there is too much strain (can't have *trans* double bond in small rings).

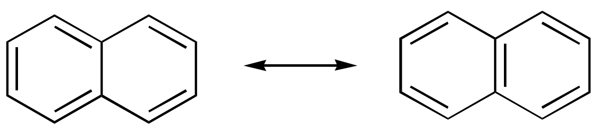


Cyclodecapentaene



This molecule has 10 π electrons. It fits with 4n+2 rule (n = 2). Although it seems to be aromatic, the hydrogens shown in the figure interfere with one another, and the molecule cannot adopt a planar conformation. Therefore, it is not aromatic.

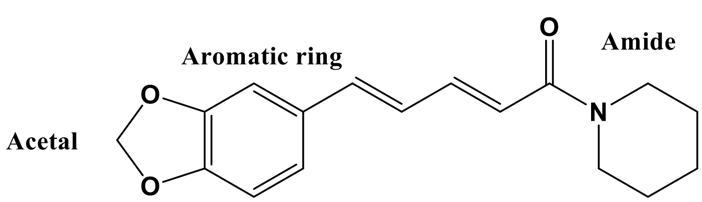
Naphthalene



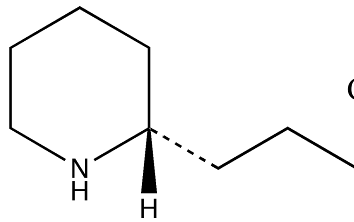
This molecule has 10 π electrons. It fits with 4n+2 rule (n = 2), and the whole molecule is planar. Therefore, naphthalene is aromatic.

Heterocycles (non-carbon atom in the ring)

Heterocycles are cyclic molecules with an atom other than carbon as a member of the ring. Keep in mind that this is a broad term, and it includes lots of molecules that may or may not be aromatic.



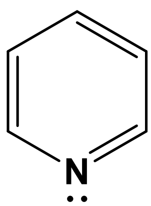
Example: Piperine from *Piper nigrum*

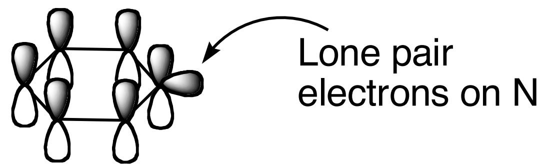


Coniine

Coniine is a heterocycle compound produced by poison hemlock. It is a neurotoxin.
Is this compound aromatic?
Answer: No. It is not conjugated since there are no double bonds present in the molecule.

Pyridine

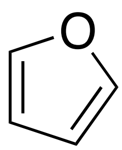


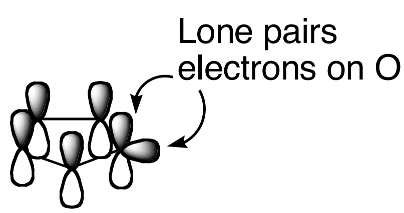


Pyridine is a heterocyclic compound. It is planar, conjugated and has 6 π electrons (4n + 2, where n = 1).

The lone pair on the nitrogen does not participate in electron delocalization within the ring since there are already 6 π electrons. Instead, the lone pair is perpendicular (90 degrees) to the p orbitals (π system) and in the plane of the ring and its hydrogens.

Furan

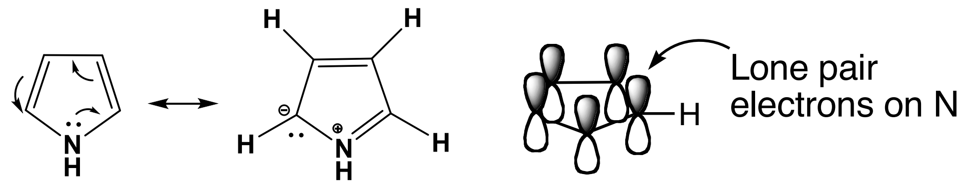




Furan is a heterocyclic compound. It is planar and has conjugated double bonds. Furan is also an aromatic compound.

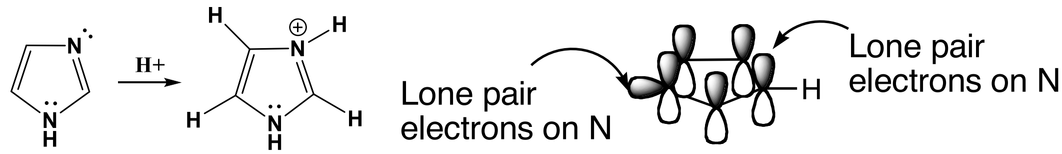
How? One of the lone pairs of electrons on the oxygen is conjugated into the ring system. The *p* orbitals of the double bonds are conjugated with one another. The oxygen arranges itself geometrically such that one of the lone pairs on the oxygen is also parallel to the *p* orbital of the double bonds, and the electrons are conjugated. The other lone pair will stick out of the ring like the hydrogens on the double bonds. Within the conjugated system, there are 6 π electrons.
(Molecules orient themselves to be and be aromatic if they can, because aromaticity gives extra stabilization).

Pyrrole



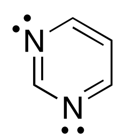
Is the molecule aromatic?
Answer: Yes. Pyrrole, similar to furan, has a lone pair of electrons (on the nitrogen) that participates in conjugation with the double bonds. There are total of 6 π electrons.

Imidazole

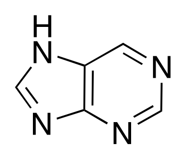


This compound is aromatic. Like pyrrole, the lone pair on the nitrogen bearing a hydrogen participates in the aromatic system. The other nitrogen without the hydrogen has its lone pair at a right angle to the π system (as in pyridine). It is this nitrogen that is more easily protonated because doing so doesn't destroy the aromatic system. Imidazole is part of the amino acid histidine.

Aromatic heterocycles and ions



pyrimidine



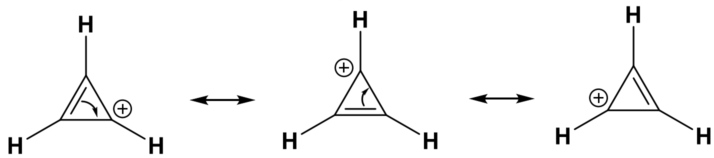
purine

Pyrimidine has 6 π electrons, and the two lone pairs of electrons on the N's are on the outside of the ring (i.e., they are not part of the conjugated system. It is an aromatic compound.

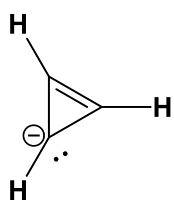
Compounds like purine are fused heterocyclic rings and are also aromatic compounds. Only the lone pair on the nitrogen bearing a hydrogen participates in the aromatic system in purine.

Aromatic Intermediates: Cations and anions

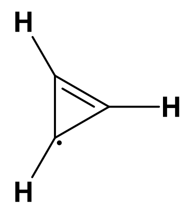
Cyclopropane and cyclopropene are extremely reactive compounds due to angle strain. The normal preferred angle of an alkane is 109° and for a double bond is 120°. In both of these molecules, the internal angle is 60°. They are highly strained.
When cyclopropene undergoes oxidation, it forms a cyclopropenium cation.



Aromatic cation: has 2π electrons



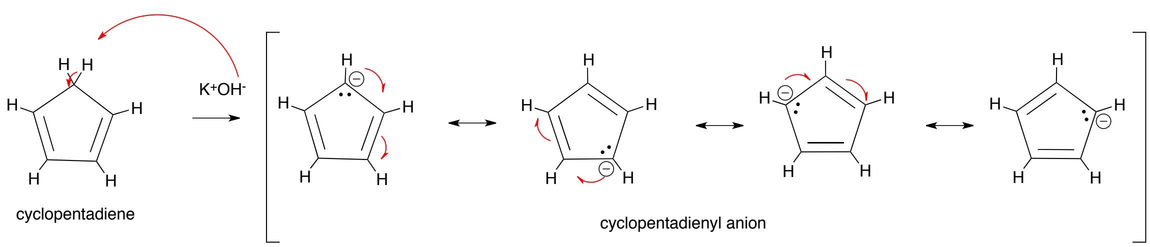
Anion: not aromatic (4π electrons)



Radical: not aromatic

Is this cation aromatic?
Answer: Yes. This molecule is cyclic, planar, conjugated, has $4n + 2$ π electrons ($n = 0$).

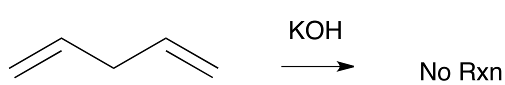
Consider another system:



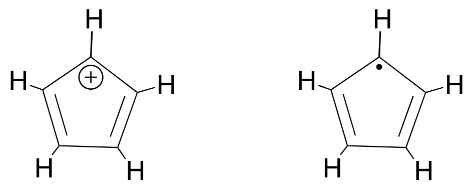
Is cyclopentadienyl anion aromatic?

Answer: Yes. It is cyclic, planar, and conjugated. It has 6 π electrons (therefore it fits the $4n + 2$ rule where $n = 1$).

The pKa of the hydrogen shown on the parent cyclopentadiene on the above figure is around 16. A normal alkane hydrogen pKa is around 45.



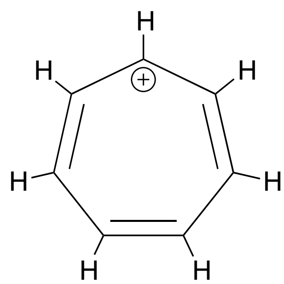
The acidity of the cyclopentadiene hydrogen has been enhanced by 30 orders of magnitude (30 pKa units) due to the extra stability of the cyclopentadienyl anion (recall that the acidity of a molecule depend on the stability of its conjugate base).



Are the cyclopentadienyl cation and radical aromatic?

Answer: No. They are cyclic, planar, conjugated, but do not follow the 4n+2 rule.

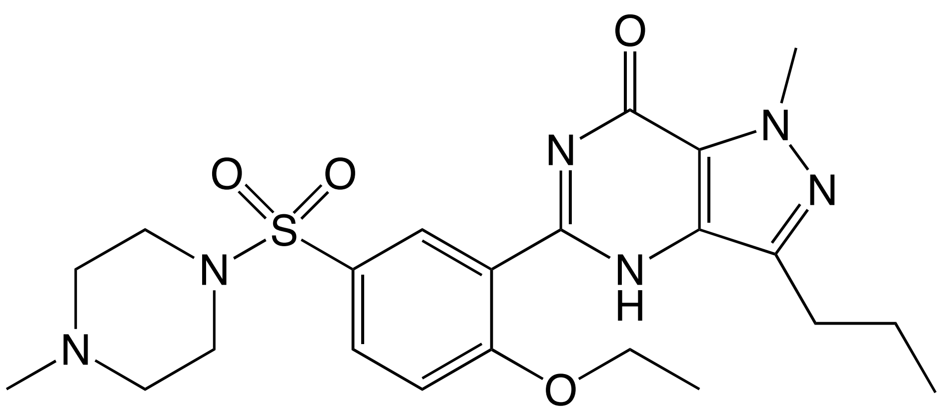
Another example:



Is this cycloheptatrienyl cation aromatic?

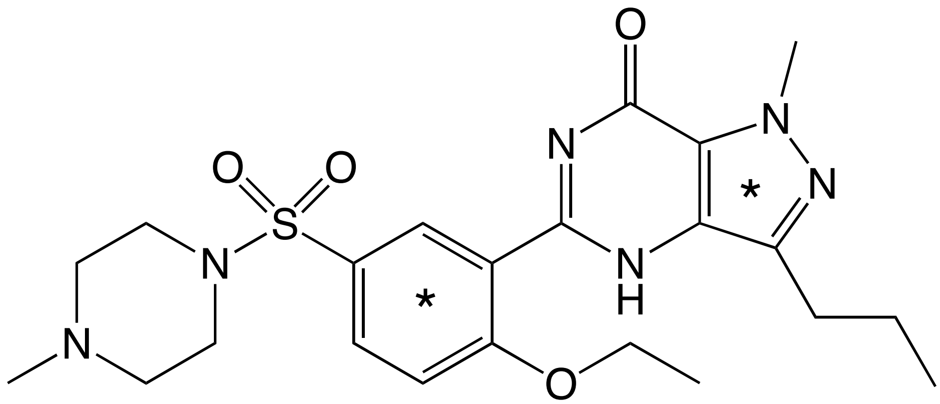
Answer: Yes, it is. The cation is cyclic, planar, fully conjugated, and has 6 π electrons. The electrons are delocalized in the ring, and each carbon shares 1/7 positive charge.

Some things you should know: Functional groups and structure



The molecule shown is **Viagra**. It generates more than $ 2.3 billion U.S. per year. Amongst other things, it aids jet lag recovery in hamsters.

Can you recognize its functional groups?



Are the rings with asterisk aromatic?

Answer: Yes. The 5-membered ring is cyclic, it has two double bonds (4 pi electrons) that are conjugated and the methyl-substituted nitrogen donates its lone pair into the 5-member ring to fit the 4n+2 rule. The other nitrogen has its lone pair in an sp^2 orbital perpendicular to the pi (π) system.

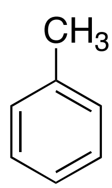
What is the molecular formula? ($C_{22}H_{30}N_6O_4S$)

Are there any stereogenic centres? (No)

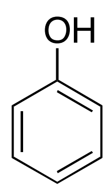
If given a molecule, know how to analyze its parts and functional groups on the exam.

Nomenclature of substituted benzene rings

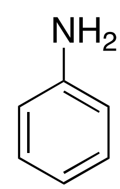
You should know the names of the following structures:



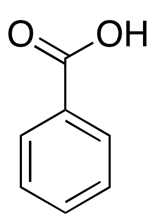
Toluene



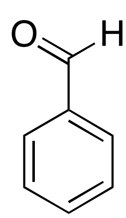
Phenol



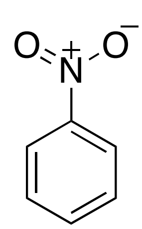
Aniline



Benzoic acid

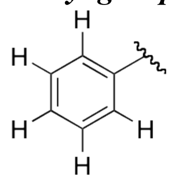


Benzaldehyde



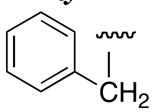
Nitrobenzene

Phenyl group = ϕ = Ph = C_6H_5

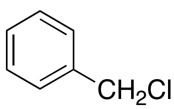


Aryl = Ar = aromatic group. It is a broad term, and includes any aromatic rings.

Benzyl = Bn =

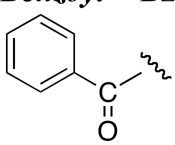


It has a $-CH_2-$ (methylene) group attached to the benzene ring.
This group can be used to name particular compounds, such as the one shown below.

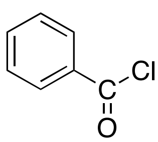


This compound has chlorine attached to a benzyl group, and is called benzyl chloride.

Benzoyl = Bz =



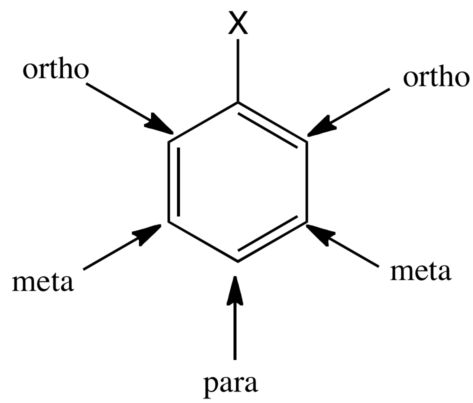
This is different from the benzyl group. It has a carbonyl attached to the benzene ring instead of a methylene group.



is named benzoyl chloride.

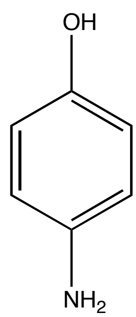
It is sometimes useful to name a compound with the aromatic part as a substituent rather than it forming a part of the parent name.

When you have two substituents on a benzene ring, *ortho*, *meta*, and *para* are used to tell where the second substitution is relative to the first one.



Ortho refers to 1,2-substitution and is abbreviated o-
Meta refers to 1,3-substitution and is abbreviated m-
Para refers to 1,4-substitution and is abbreviated p-

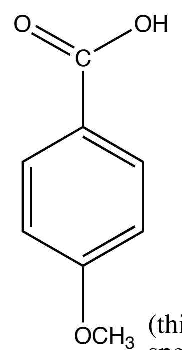
Examples:



p-aminophenol
(more correct, OH has priority)

or

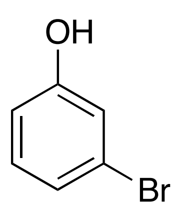
p-hydroxyaniline



p-methoxybenzoic acid

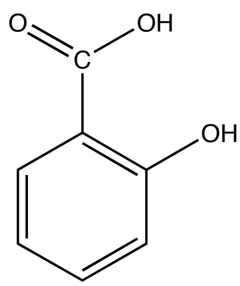
(this is an ether group, specifically methoxy)

Nomenclature: p-aminophenol or 4-aminophenol:
The amine and hydroxyl group are in the 1 and 4 positions, so they are *para* to each other. The parent structure in this molecule can be either aniline or phenol. For this course, it doesn't matter which parent structure you pick in the nomenclature with these substituents. Usually when naming the substituents, the atomic number takes priority, but there are many exceptions for historical reasons.

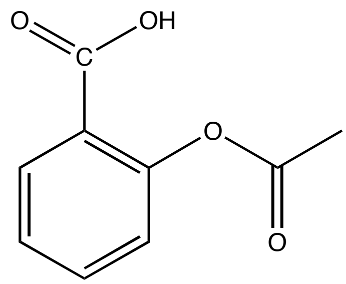


Nomenclature: *m*-bromophenol or 3-bromophenol
In this compound, the –OH (hydroxy) and –Br are in the 1 and 3 positions, so they are *meta* (or abbreviated *m*) to each other. The parent structure is phenol (phenol is a benzene

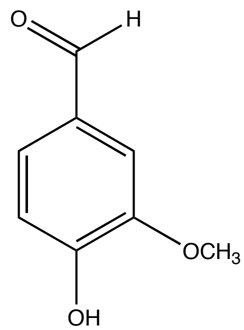
with a hydroxyl group directly attached, not to be confused with phenyl which means just a benzene ring as a substituent), so we call this meta-bromophenol.



2-hydroxybenzoic acid
aka salicylic acid

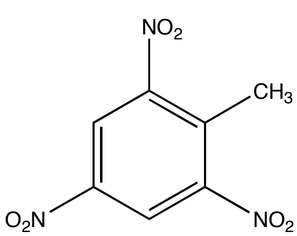


aspirin
acetylsalicylic acid

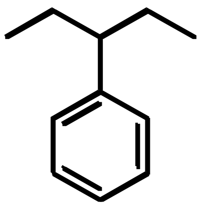


Nomenclature: 4-hydroxy-3-methoxybenzaldehyde (or vanillin from vanilla extract). The carbon substituent (an aldehyde group) gets priority.

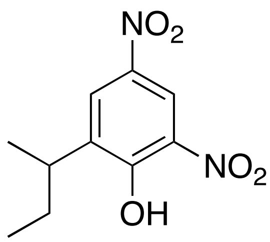
Note: we number the ring in a way such that the substituents have the lowest numbers (so it's not 4-hydroxy-5-methoxy-, but 4-hydroxy-3-methoxy-). The substituents are listed in alphabetical order before the parent compound, but this course will not be incredibly picky with the order.



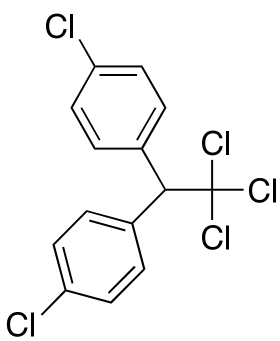
Nomenclature: 2,4,6-trinitrotoluene (TNT)
An explosive



Nomenclature: 3-phenylpentane (pentan-3-ylbenzene is also an acceptable name, but it is more complicated and isn't the best name). (Note that this molecule is achiral: it has a plane of symmetry)

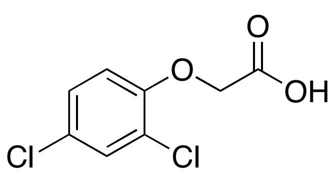


This is Amaize. It is used to enhance the yield of corn production.
The systematic name for this compound is 2-*sec*-butyl-4,6-dinitrophenol. It can also be called 6-(1-methylpropyl)-2,4-dinitrophenol.

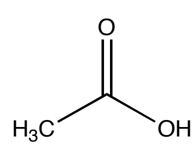


1,1,1-trichloro-2,2-bis-(4-chlorophenyl)ethane
Note: Although the two 4-chlorophenyl can also be named using di-, bis is used instead. bis is commonly used for large groups. The 4-chlorophenyl could also be called p-chlorophenyl

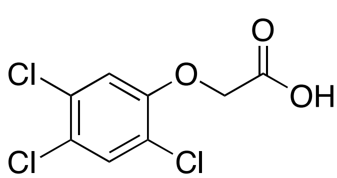
This compound is commonly known as DDT. DDT is an insecticide and helped to wipe out malaria in many parts of the world. The person who discovered its properties (Paul Müller) won the Nobel Prize in Medicine in 1948.



2,4-dichlorophenoxyacetic acid (2,4-D)

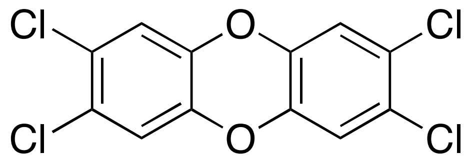


Note: Acetic acid
is the parent structure

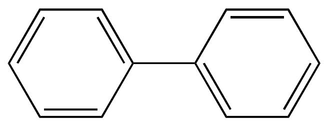


2,4,5-trichlorophenoxyacetic acid (2,4,5-T)

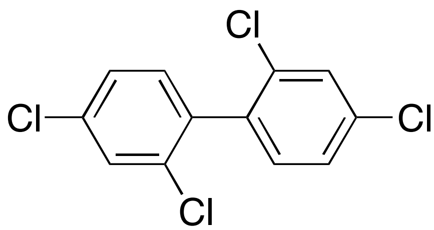
Agent Orange (2,4-D + 2,4,5-T), a broad leaf herbicide, was used in the Vietnam War to defoliate large areas. It was used in Edmonton on lawns as "Weed and Feed".



Dioxin is a potent toxin and carcinogen that can contaminate Agent Orange and can occur in pulp mill waste. While this is only an example of one dioxin, typically the term dioxin refers to this particular molecule.



biphenyl



A polychlorinated biphenyl (PCB). PCBs were used in electrical transformers and are persistant organic pollutants.

If the Cl's were Br's this would be a polybrominated biphenyl (PBB).