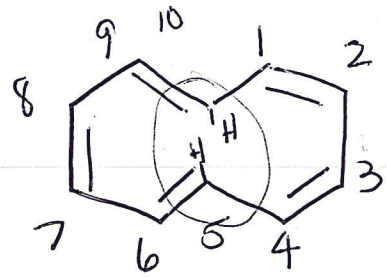
15.5

I.



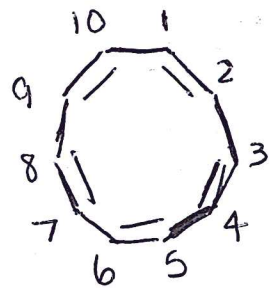
1,3,5,7,9-Cyclopentaene

In order for compounds to be aromatic, they must meet <u>all</u> four of the following criteria

- CYCLIC
- PLANAR
- CONTINUOUS π SYSTEM
- $4n+2 = \#\ \pi\ e^{\ominus}$

n = integer

II.



(all cis π bonds)

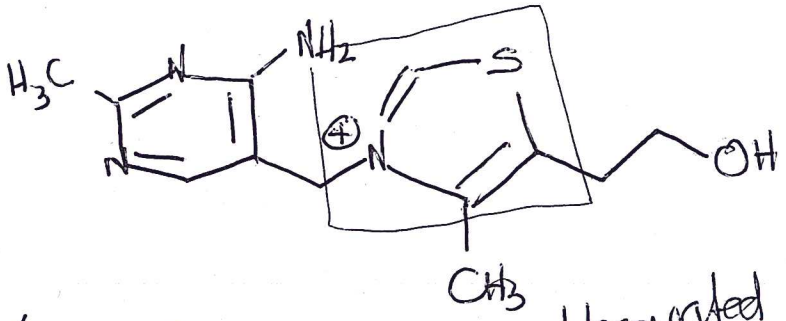
1,3,5,7,9-cyclopentaene "appears" to fulfill all 4 of the criteria for aromaticity. However the size of the ring allows the compound to be drawn in a couple of different ways, represented by structures I and II above

Structure I is actually <u>not</u> planar because the Hydrogen interactions at C_{10} and C_5 (circled) force the ring to "pucker" and perturb the planarity of the system.

15.5 (cont'd)

Structure II, with all cis π bonds has significant angle strain and will revert to structure I to relieve this angle strain (sp² carbons of the all cis structure are "forced" to adopt bond angles of 140° when the ideal bond angle is 120°)

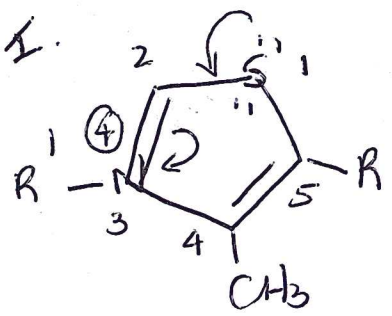
15.10



CYCLIC ✓
PLANAR ✓

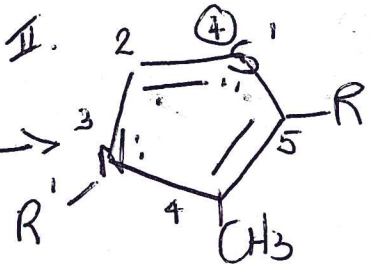
The structure is abbreviated to focus on the five-membered ring. Number the atoms of the ring and check for the four criteria for aromaticity.

I.



⟷

II.

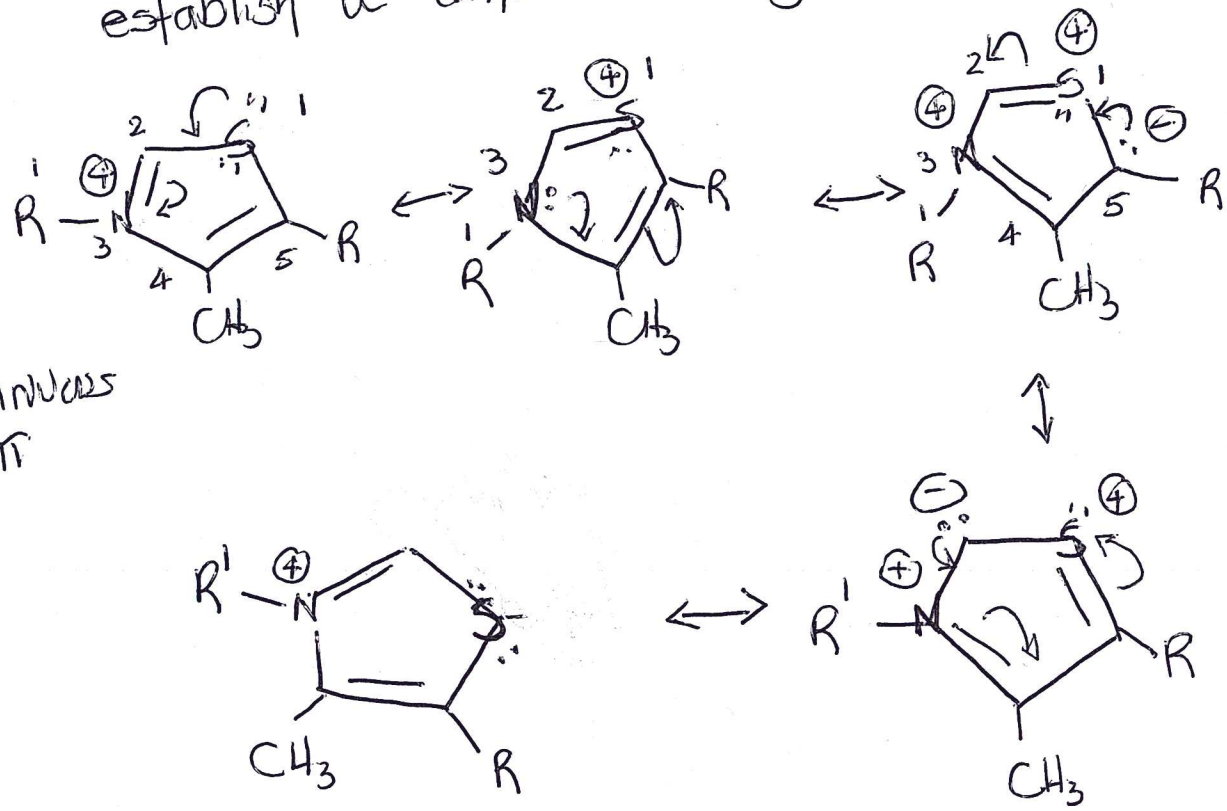


C_2, N, C_4 and C_5 are sp^2 in structure I. S, C_2, C_4, C_5 are sp^2 in structure II.

15.10 (cont'd)

All five atoms can adopt sp^2 hybridization in at least one of these resonance forms. All atoms can adopt planar geometry therefore the overall ring is planar.

Using the lone pair on the S atom, delocalize these $e^{\ominus}$ all the way around the ring to establish a continuous π system.

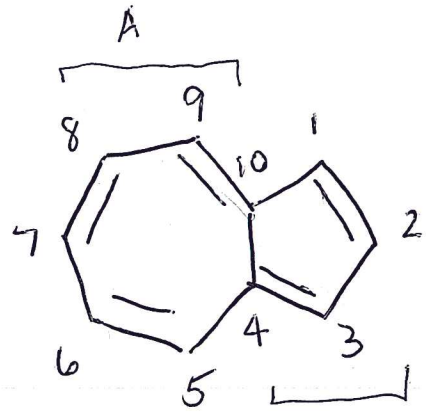


✓ continuous π

✓ $4n+2=6$
$n=1$

Since the lone pair on sulfur was used to establish the continuous π system, it is counted, along with $4e^{\ominus}$ in the π bonds to determine n in Hückel Rule

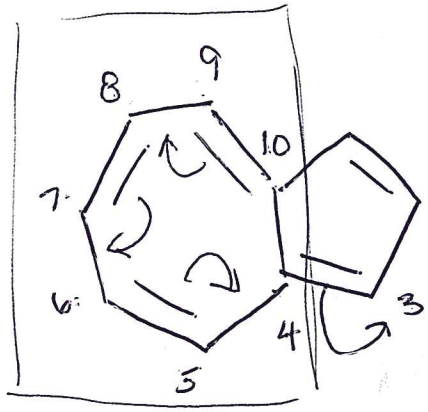
15.11



AZULENE

To show aromaticity in a fused system, check each ring individually <u>and</u> overall ring (i.e. membered ring)

<u>A</u>:



Ring A alone is not aromatic

Focus <u>only</u> on ring A

$C_4 - C_{10}$

✓ CYCLIC: (7-membered ring)

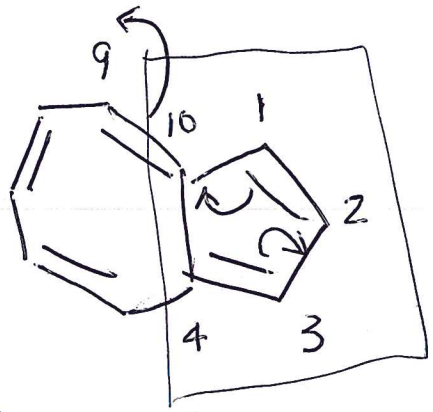
✓ PLANAR: all 7 atoms sp^2 hybridized

X CONT π: to establish continuous π, must delocalize <u>only</u> within ring A.

Since $C_4 - C_3$ π bond moves <u>out</u> of ring A, ring A <u>alone</u> does not have a continuous π system

15.11 (cont'd)

B:



Ring B alone is not aromatic

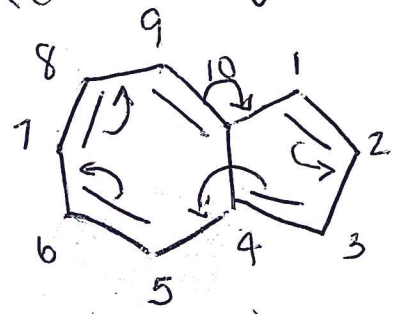
Focus only on ring B
C_1–C_4, C_{10}

✓ CYCLIC: 5-membered ring

✓ PLANAR: All 5 atoms of the ring are sp^2

✗ CONT π: C_{10}–C_9 π bond moves OUT of Ring B
NO CONT. π within ring B

C: (entire ring)



Entire ring system (A + B TOGETHER) are aromatic

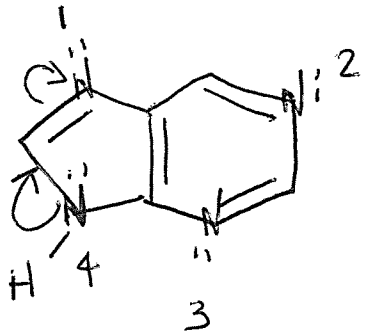
✓ CYCLIC: 10-membered ring

✓ PLANAR: All 10 atoms are sp^2 hybridized

✓ CONT π: π e⊖ can move all the way around ring

✓ $4n+2=10$ $n=2$ (integer)

15.12

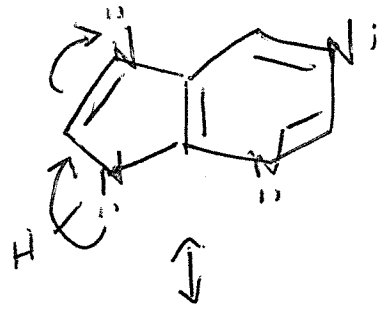


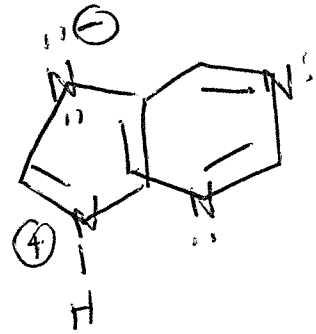
There are four nitrogen atoms in purine.

N_1, N_2, N_3 all are part of a π bond.

The lone pairs on these N atoms do not contribute to the aromatic system.

N_4 is sp^3 hybridized. Its lone pair can contribute to the π system to establish sp^2 hybridized character for this N, making the entire system planar



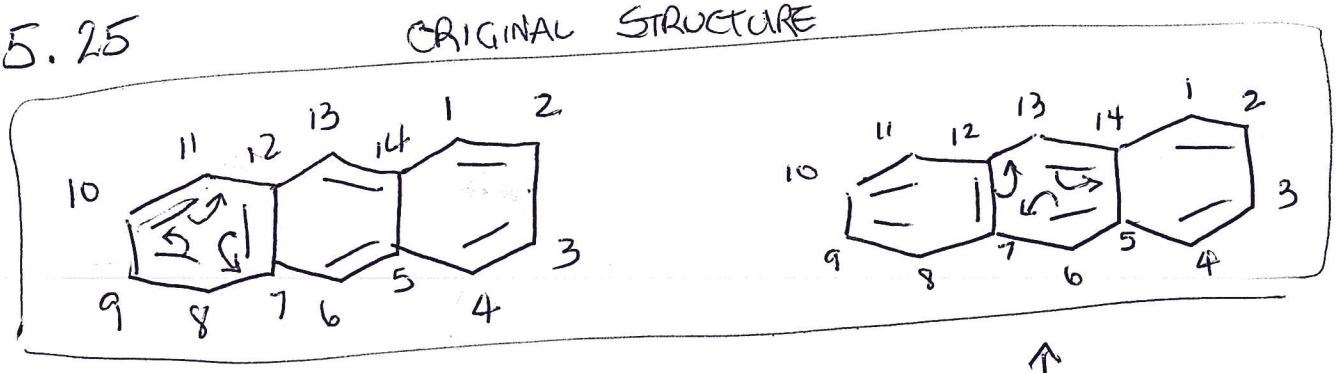


Only the lone pair on N_4 contributes to the aromatic system.

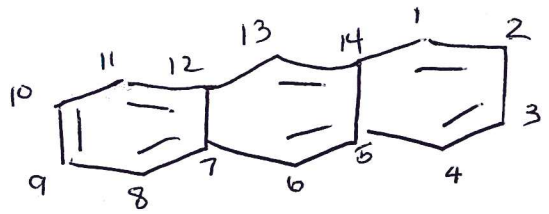
15.25

ORIGINAL STRUCTURE

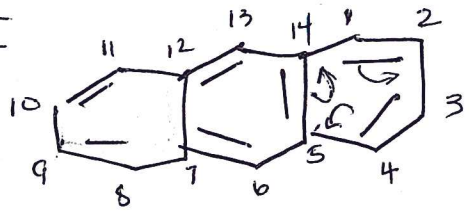
I



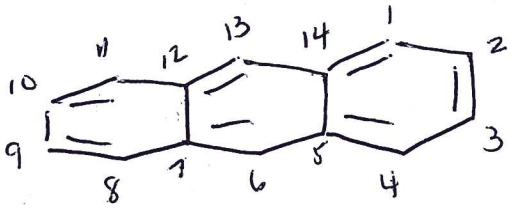
II



III



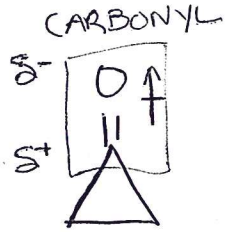
IV

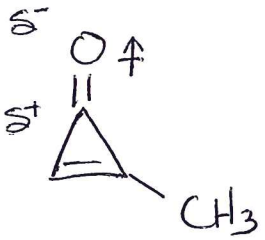


The other 3 structures are represented by II, III, IV.

15.31

CARBONYL

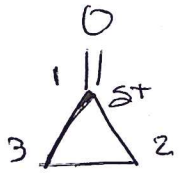




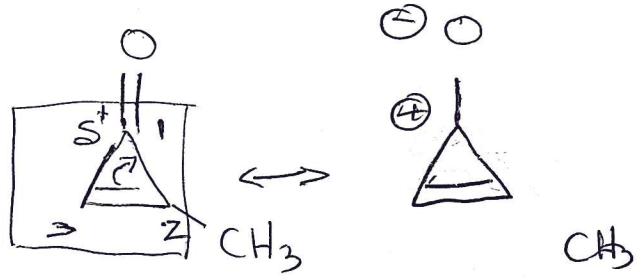
The carbonyl group is polarized with the more electronegative oxygen "pulling" electrons away from the carbon.

15.31 (cont'd)

This polarization creates a partial positive charge on the carbon atom of the carbonyl



Cyclopropanone is NOT aromatic since C_2, C_3 are sp^3 ⇒ not planar



The partial positive charge on methyl-cyclopropenone creates aromatic character in this molecule. (check criteria)
(Assume C_1 is a carbocation)

4n+2:

Only the 2 π e⁻ of the ring (carbonyl π e⁻ NOT part of ring)

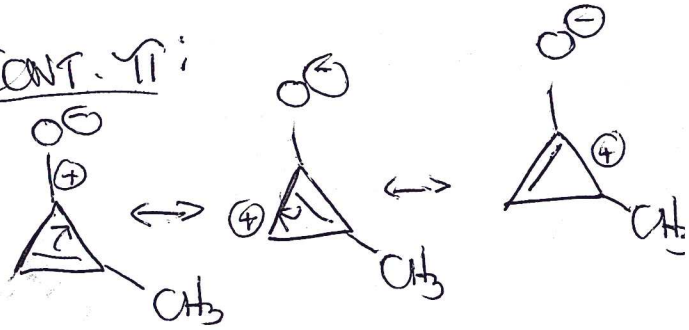
$4n+2=2$
$n=0$ (integer)

The aromatic character makes the molecule VERY stable

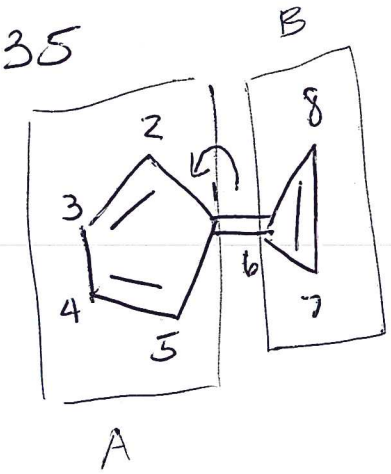
CYCLIC: 3-membered ring

PLANAR: All 3 carbons are sp^2 → planar

CONT. π:

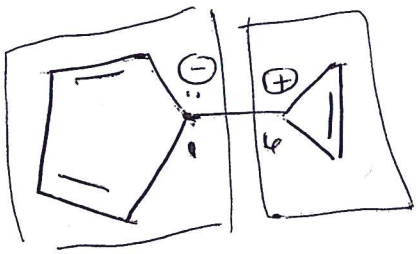


15.35



The dipole moment is localized around the C_1–C_6 bond.

Polarization of the C_1–C_8 bond induces a partial positive charge @ C_6 and a partial negative charge @ C_1



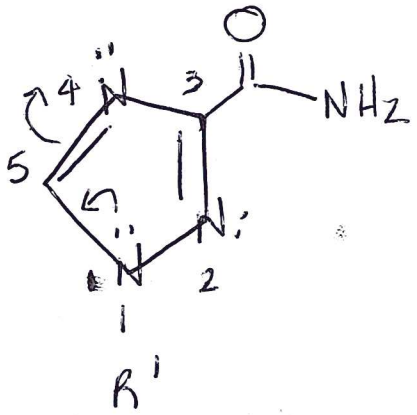
A resonance structure showing the "extreme" polarization places a positive charge at C_6, a negative charge (w/ lone pair) at C_1

If ring A in this extreme polarized resonance structure is checked for aromaticity, all criteria are met and ring A has aromatic character

Simultaneously, ring B is aromatic.

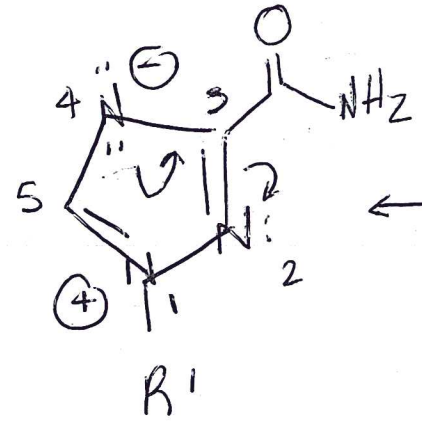
Polarization of the C_1–C_6 bond creates aromatic character in the molecule and stabilization

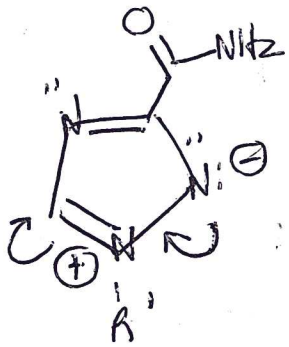
15.38 The triazole ring is abbreviated to focus on the atoms of the ring while checking criteria for aromaticity.



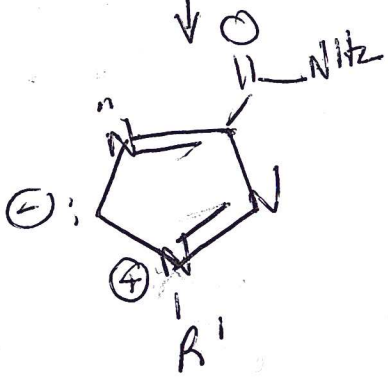
✓CYCLIC: 5-membered ring

✓PLANAR: All 5 atoms of the ring can adopt sp^2 (planar) geometry in at least 1 resonance form. Use lone pairs on N_1 to show





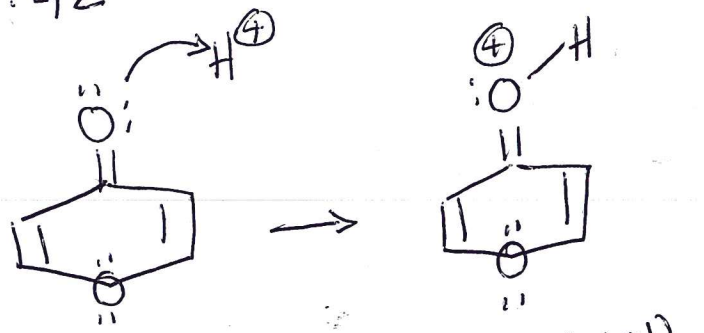
✓CONT π: Lone pair starting at N_1 can delocalize all the way around the ring.



✓ $4n+2=6$
$n=1$ (integer)

Lone pair on N_1 counted, along w/ $4e^{\ominus}$ of π bonds.

15.42



4-PYRONE

BASE

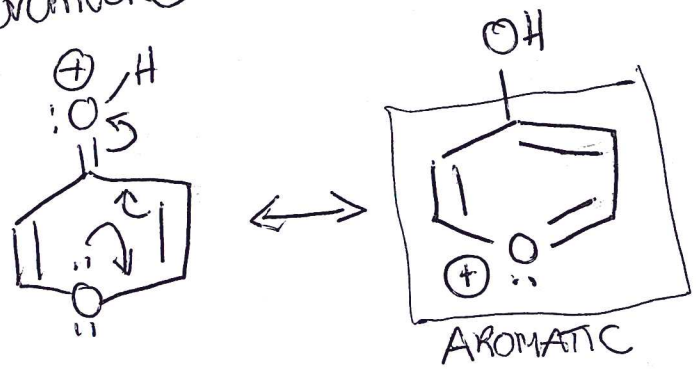
(OXONIUM ION)

CONJUGATE ACID

The oxygen atom accepts a proton to become protonated (OXONIUM ION)

The 4-pyrone behaves as a base and the resulting oxonium ion is the CONJUGATE ACID

If a resonance form of the oxonium ion is drawn and evaluated for aromaticity, it is determined that this CONJUGATE ACID is aromatic

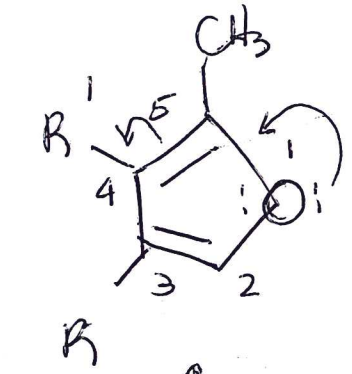


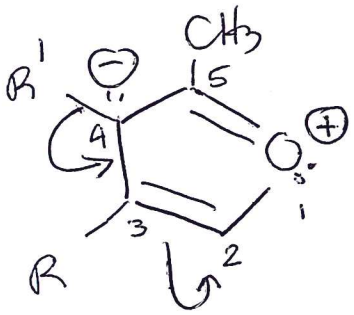
AROMATIC

The aromatic character of the conjugate acid makes it VERY STABLE

15.43

Abbreviate the structure to focus on the isoxazole ring of Bextra. Number the atoms of the ring and check criteria for aromaticity

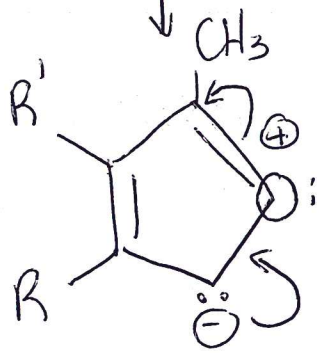


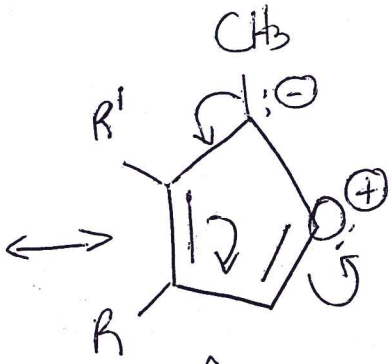


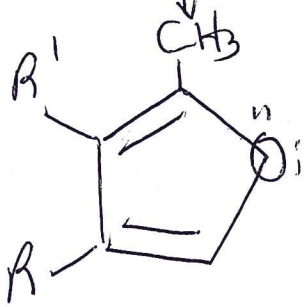
✓ CYCLIC: 5-membered ring

✓ PLANAR: All atoms in ring can adopt sp^2 (planar) geometry in at least one resonance form

✓ CONT. π: Lone pair on oxygen can delocalize all the way around the ring



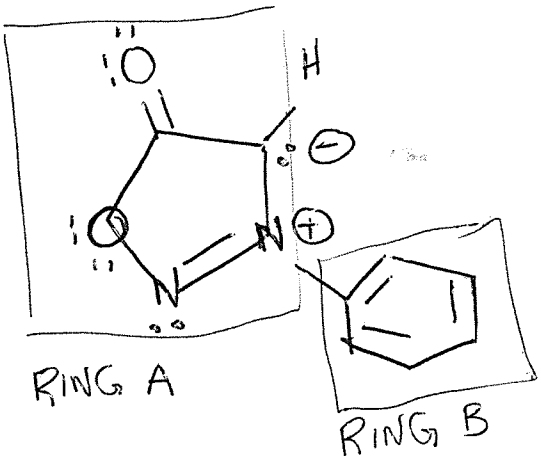




✓ $4n+2=6$
$n=1$ (integer)

Use the lone pair on oxygen and the 4 e⊖ of the π bonds

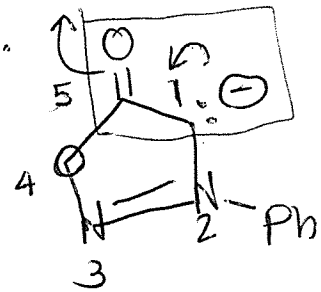
15.44. There are two rings in the structure of N-phenylsydnone. The benzene ring (B) is obviously aromatic. The question is, is ring A also independently aromatic.



Abbreviate the structure to focus on ring A.

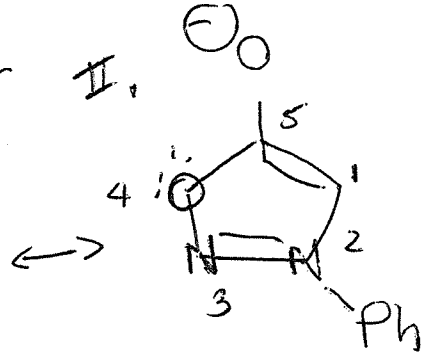
Check ring A for aromaticity criteria

I.



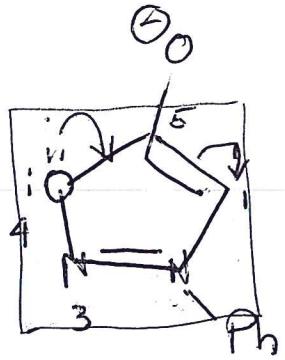
Delocalize lone pair on C_1 up through carbonyl π bond

II.



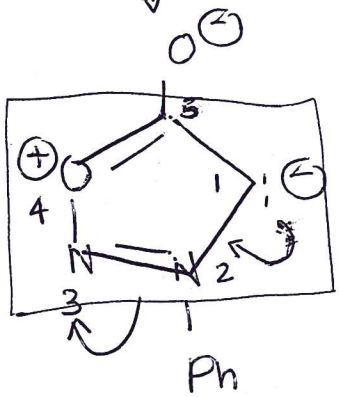
Once this structure (II) is generated check aromaticity criteria

15.44 (cont'd)

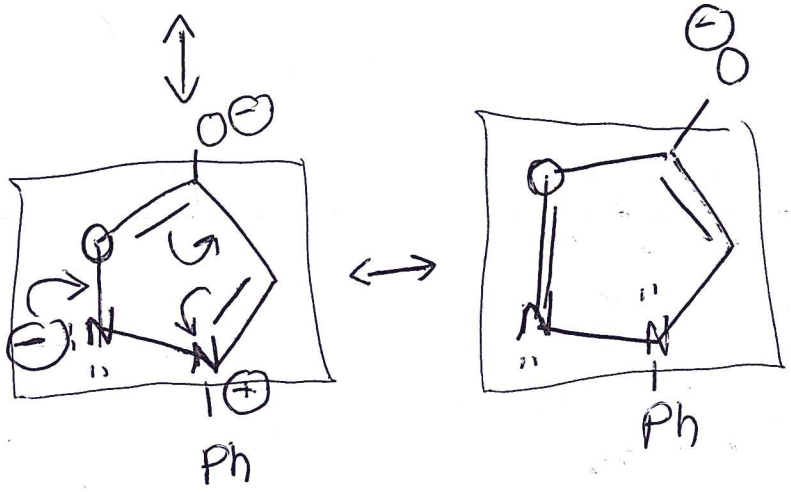


✓ CYCLIC: 5-membered ring

✓ PLANAR: All 5-atoms of the ring can adopt sp^2 (planar) hybridization in at least one resonance form.



CONT π: Lone pair from oxygen can delocalize all the way around the ring.



$4n+2=6$ $n=1$

Count <u>only</u> $e^{\ominus}$ in the ring (<u>NOT</u> $e^{\ominus}$ out on the oxygen outside the ring)

2 $e^{\ominus}$ from oxygen <u>IN THE RING</u> and 4 $e^{\ominus}$ from π bonds