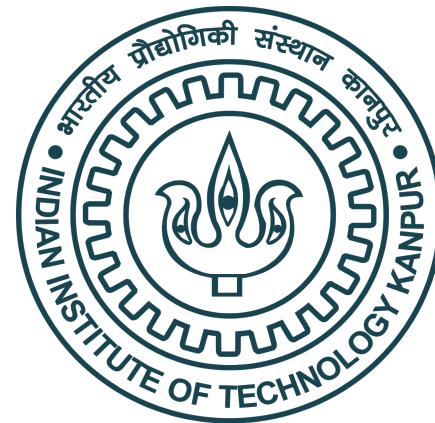


Lecture 8-10

Organic Chemistry: Fundamentals and Applications (CSO201A)



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NOMENCLATURE OF HETEROCYCLIC COMPOUND



The IUPAC rules allow three
nomenclatures

I. Common Names

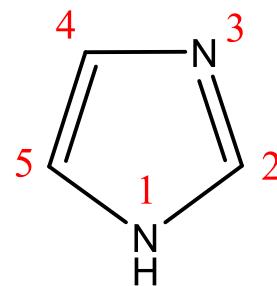
II. The Replacement Nomenclature

III. The Hantzsch-Widman Nomenclature



I-Common Nomenclature

- ✓ Each compound is given the corresponding trivial name. This usually originates from the compounds occurrence, its first preparation or its special properties.
- ✓ If there is more than one hetero atom of the same type numbering starts at the saturated one, e.g. imidazole.

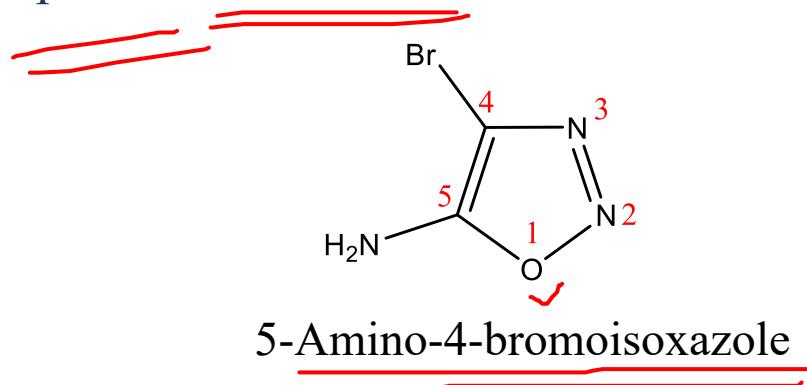


- ✓ If there is more than one type of the hetero atoms, the ring is numbered starting at the hetero atom of the higher priority (O>S>N) and it continues in the direction to give the other hetero atoms the lower numbers as possible.

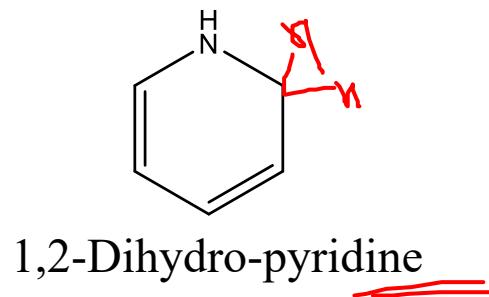


I-Common Nomenclature

- ✓ If substituents present, their position should be identified by the number of the atoms bearing them and then they should be listed in alphabetical order.

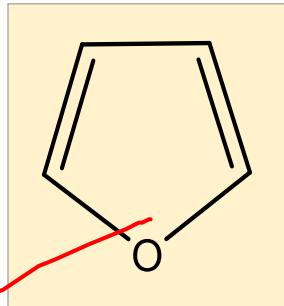


- ✓ The words **dihydro** or **trihydro** or **tetrahydro** are used if two or three or four atoms are saturated. These words are preceded by numbers indicate the position of saturated atoms as low as possible and followed by the corresponding fully unsaturated trivial name.

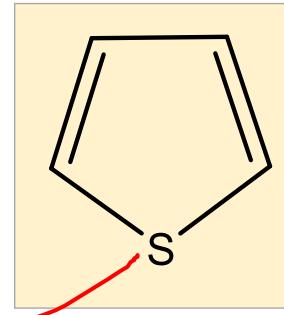


I-Common Nomenclature

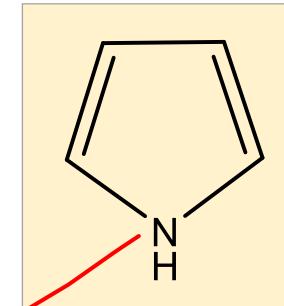
- ✓ 5-membered heterocycles with one or two heteroatoms



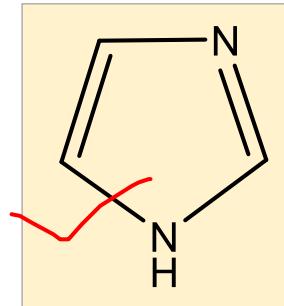
Furan



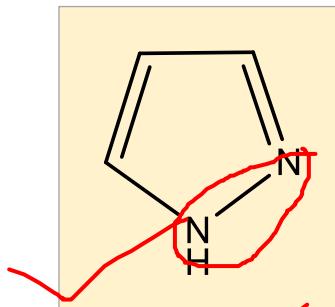
Thiophene



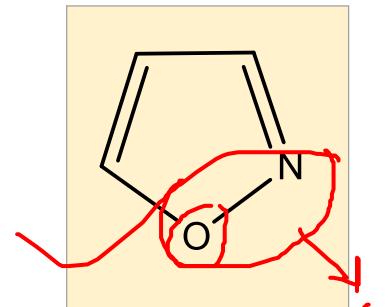
Pyrrole



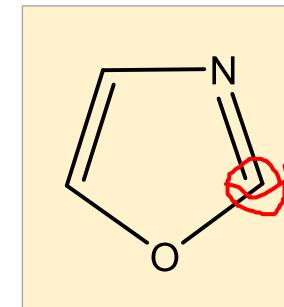
Imidazole



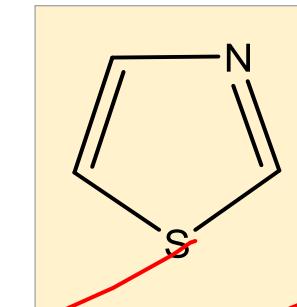
Pyrazole



Isoxazole



Oxazole

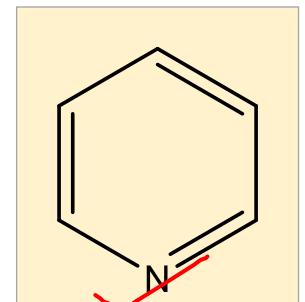
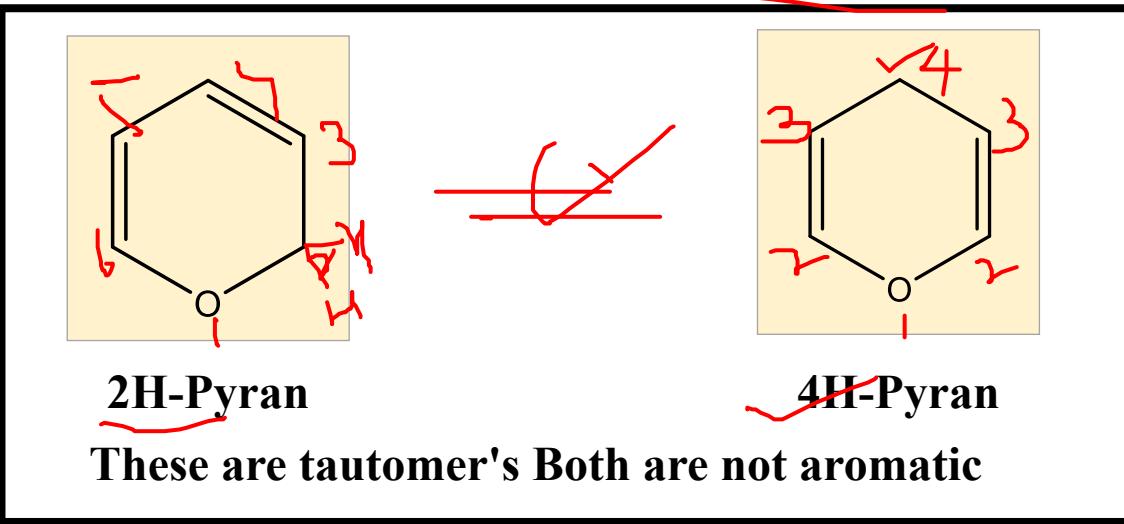


Thiazole

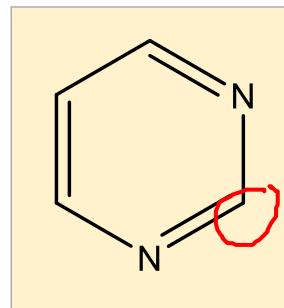


I-Common Nomenclature

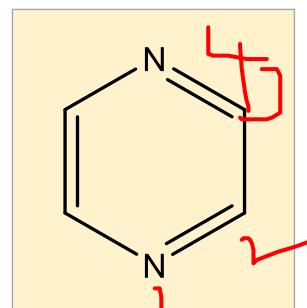
✓ 6-membered heterocycles with one or two heteroatoms



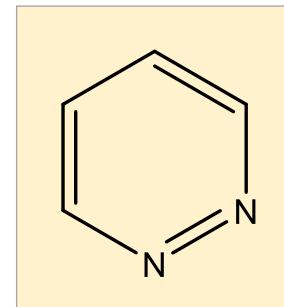
Pyridine



Pyridazine



Pyrimidine
DNA/RNA bases

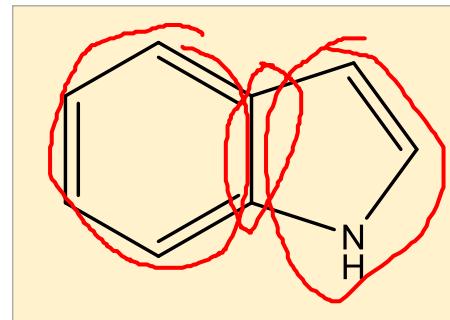


Pyrazine

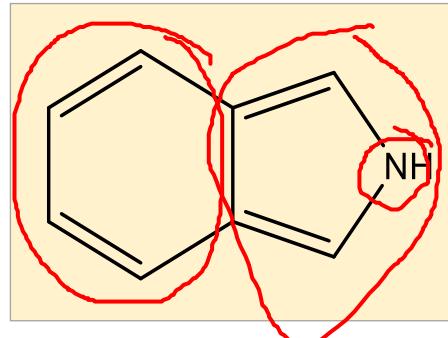


I-Common Nomenclature

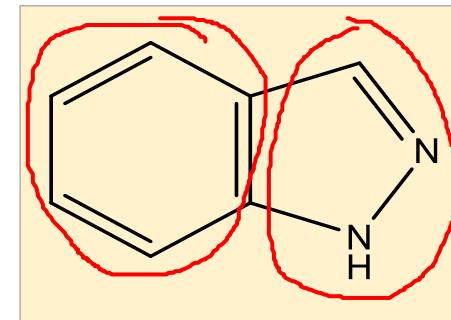
✓ Fused heterocycles



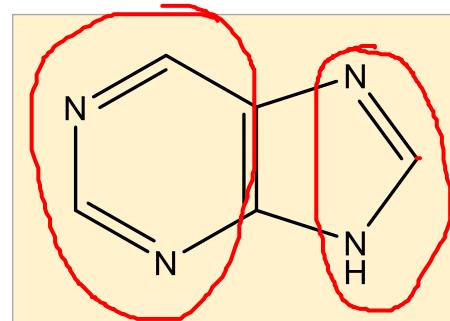
Indole



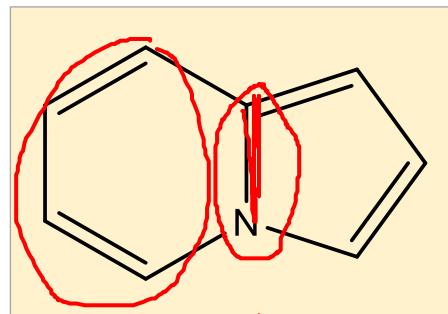
Isoindole



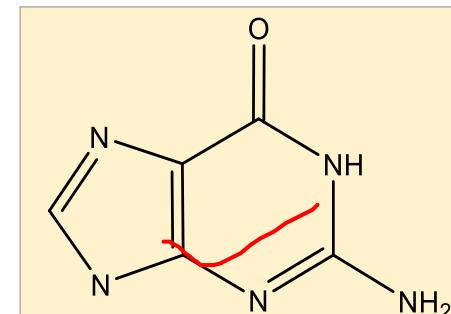
Indazole



Purine



Indolizidine

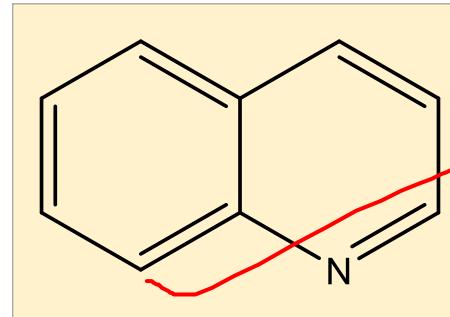


Guanine

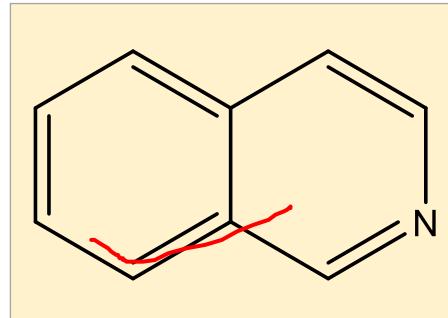


I-Common Nomenclature

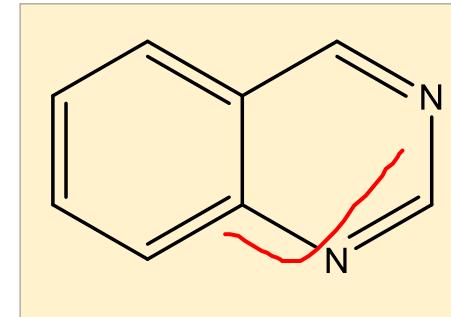
✓ Fused heterocycles



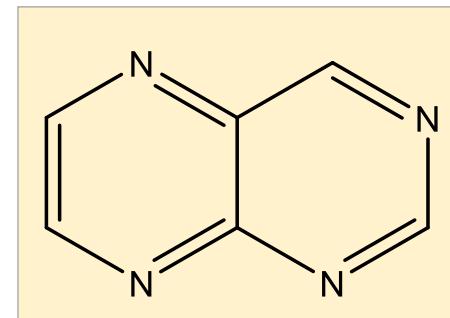
Quinoline



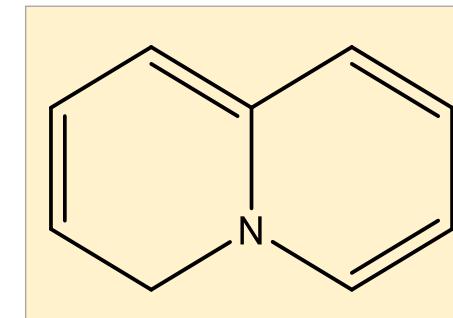
Isoquinoline



Quinazoline



Pteridine

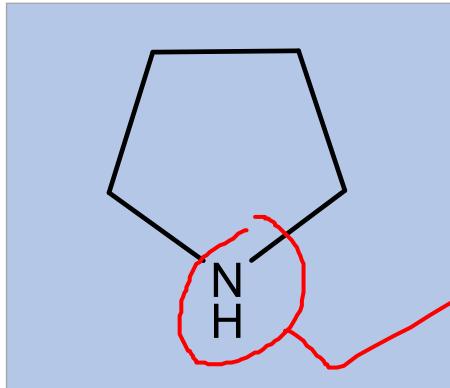


Quinolizidine

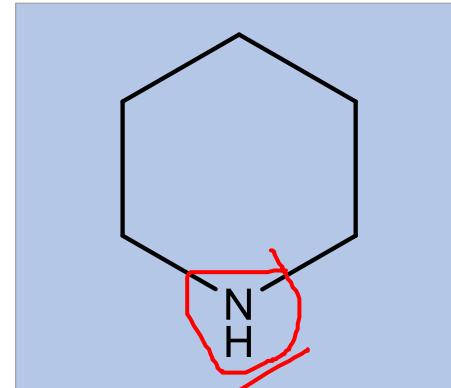


I-Common Nomenclature

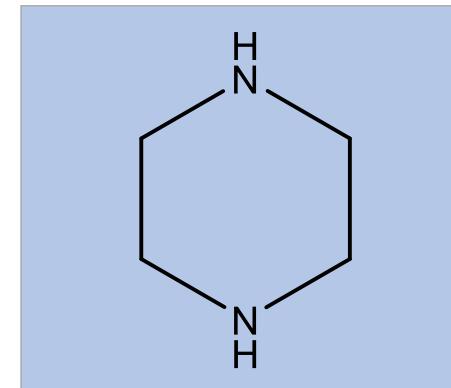
✓ Saturated heterocycles



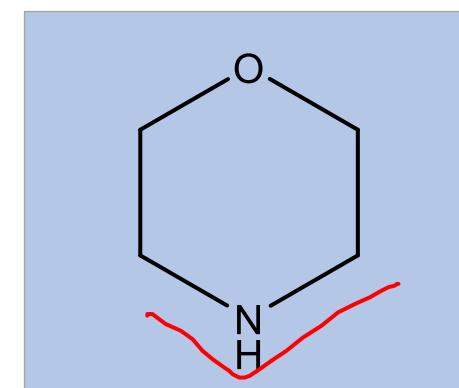
Pyrrolidine



Piperidine



Piperazine



Morpholine



II-Replacement nomenclature

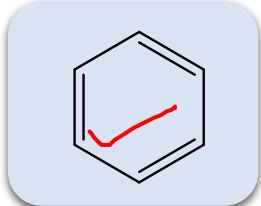
- ✓ Heterocycle's name is composed of the corresponding carbocycle's name and an elemental prefix for the hetero atom introduced, If more than one hetero atom is present they should be listed according to the priority order shown in table
- ✓ Notice that heterocyclic rings are numbered so that the heteroatom has the lowest possible number.

ATOM	PREFIX
O	Oxa
S	Thia
Se	selena
N	Aza
P	Phospha

PRIORITY
DECREASE

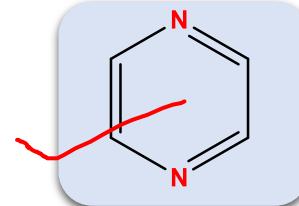


II-Replacement nomenclature



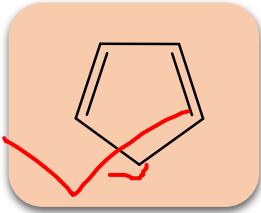
Benzene

====

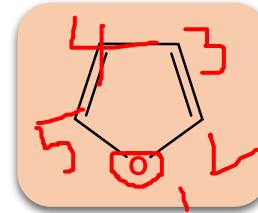


1,4-Diazabenzene

=====

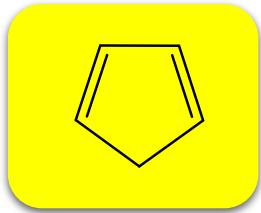


Cyclopentadiene



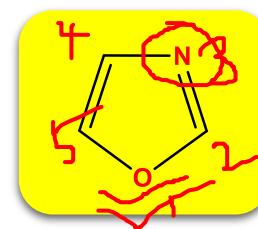
Oxacyclopenta-2,4-diene

=====



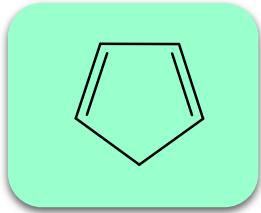
Cyclopentadiene

=====

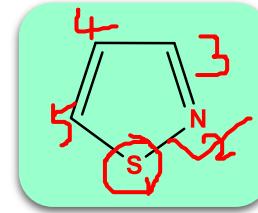


1-Oxa-3-azacyclopenta-2,4-diene

=====



Cyclopentadiene

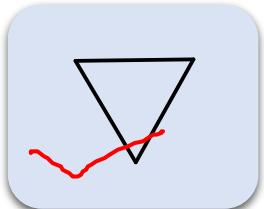


1-Thia-2-azacyclopenta-2,4-diene

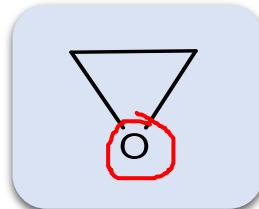
=====



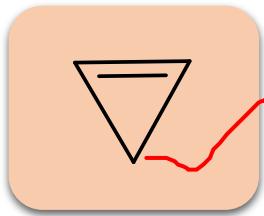
II-Replacement nomenclature



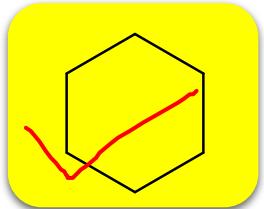
Cyclopropane



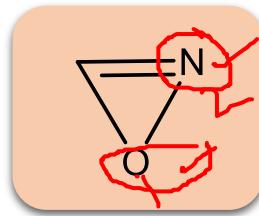
Cyclopropane



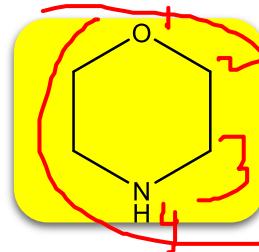
Cyclohexane



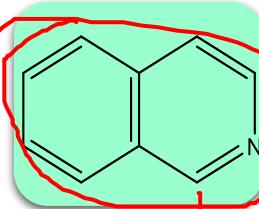
Naphthalene



Oxacyclopropane



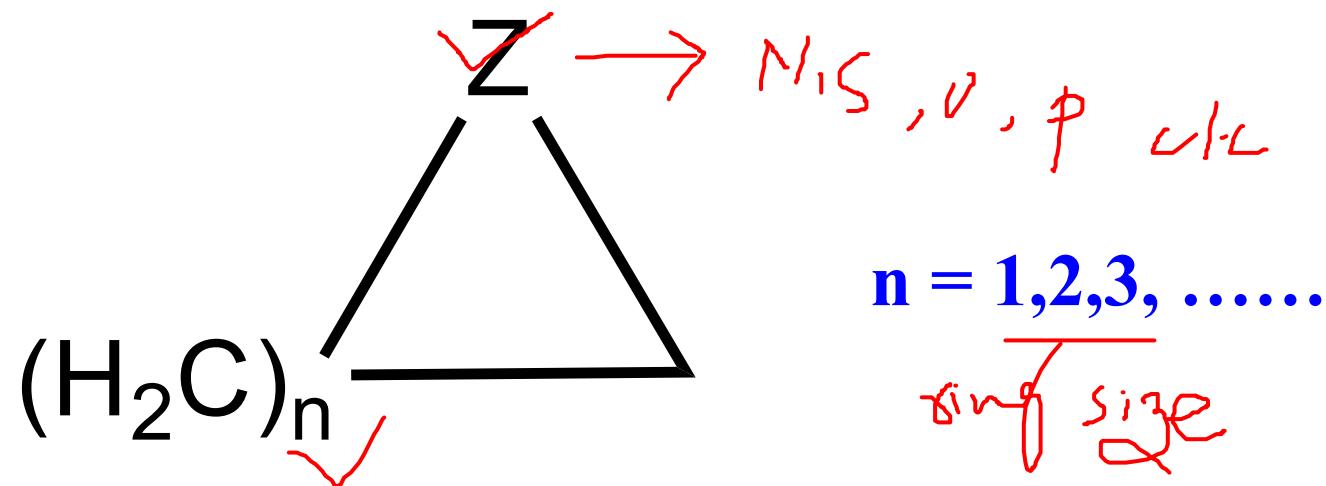
1-Oxa-4-azacyclohexane



2-Azanaphthalene



III. Hantzsch-Widman Nomenclature



- ✓ German chemists Arthur Hantzsch and Oskar Widman, proposed similar systematic naming of heterocyclic compounds in 1887 and 1888 respectively
- ✓ The Hantzsch-Widman nomenclature is based on the type (Z) of the heteroatom; the ring size (n) and nature of the ring, whether it is saturated or unsaturated.
- ✓ This system of nomenclature applies to monocyclic three-to-ten-membered ring heterocycles.



Hantzsch-Widman rules for fully saturated and fully unsaturated heterocycles

- ✓ IUPAC name = locants+ prefix +suffix ✓
- ✓ Identify the hetro atom present in the ring and choose from the corresponding prefix

ATOM	PREFIX
O	Oxa
S	Thia
Se	selena
N	Aza
P	Phospha

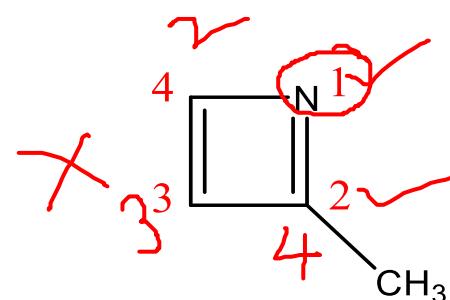
PRIORITY
DECREASE



Hantzsch-Widman RULE

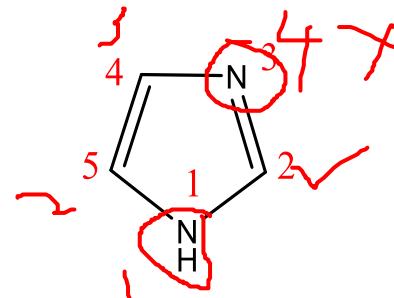
- ✓ The position of a single heteroatom control the numbering in a monocyclic compound. The heteroatom is always assigned position 1 and if substituents present are then counted around the ring in a manner so as to take the lowest possible numbers.

For example,



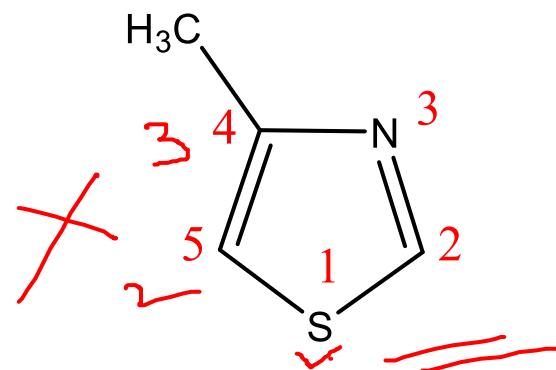
- ✓ A multiplicative prefix (di, tri, etc.) and locants are used when two or more similar heteroatoms contained in the ring(two nitrogen indicated by di aza) and the numbering preferably commenced at a saturated rather than an unsaturated atom, as depicted in the following

For example, 1,3- diaza....



Hantzsch-Widman RULE

- ✓ If more than one type of hetero atoms present in the ring the name will include more than one prefix with locants to indicate the relative position of the heteroatoms.
- When combining the prefixes (e.g. oxa and aza) two vowels may end up together, therefore the vowel on the end of the first part should be omitted (oxaza).
- The numbering is started from the hetero atom of the highest priority in such a way so as to give the smallest possible numbers to the other hetero atoms in the ring (the substituents are irrelevant). For example the prefix corresponding to the following compound is **4-Methyl-1,3-thiaza....**



S - 1
N - 2



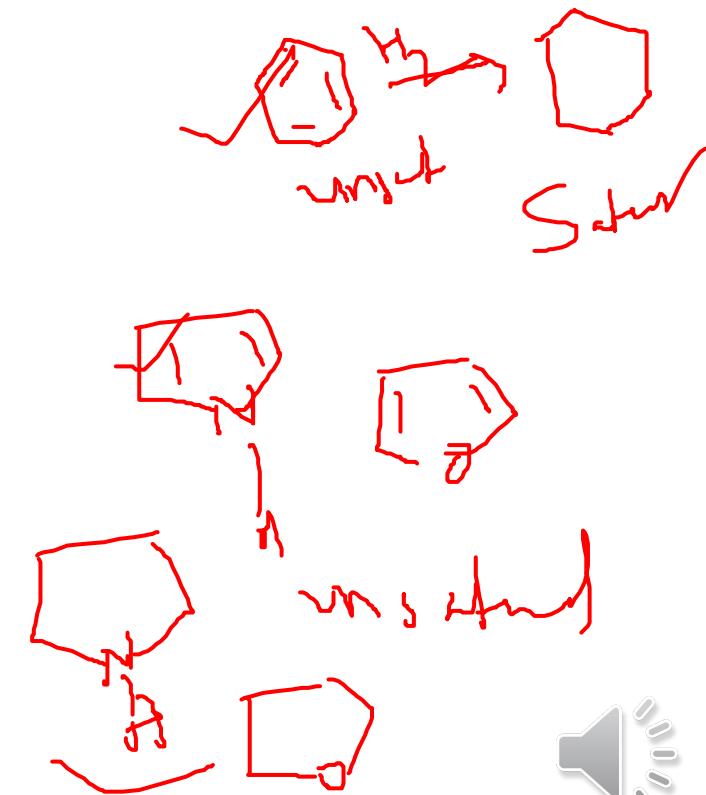
Hantzsch-Widman RULE

- ✓ Choose the appropriate suffix from depending on whether or not nitrogen atom is present in the ring, the size of the ring and presence or absence of any double bonds



N PRESENT

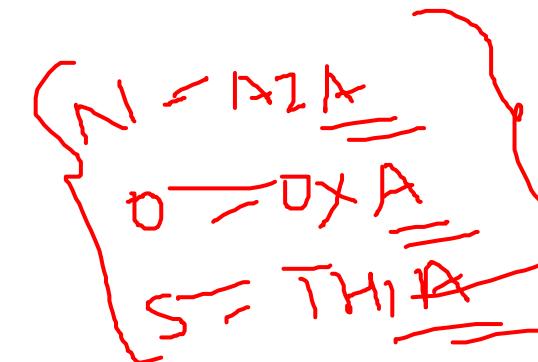
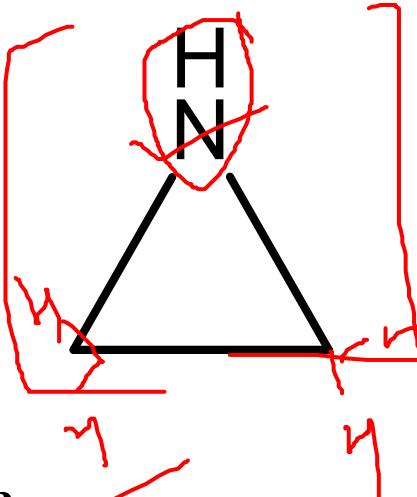
Ring size	Unsat	Sat
3	Irine	Iridine
4	Ete	Etidine
5	ole	olidine
6	Ine	A
7	Epine	A
8	Ocine	A
9	Onine	A
10	Ecine	A



Hantzsch-Widman RULE

- ✓ Combine the prefix(s) and suffix together and drop the first Hantzsch -Widman rules vowel if two vowels came together.

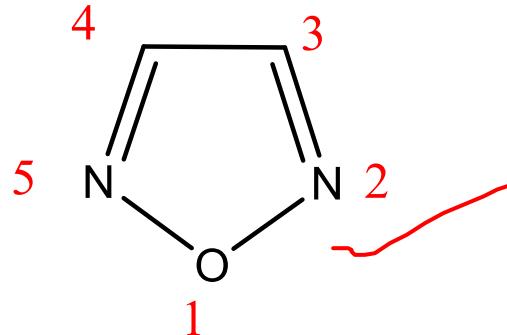
For example,



- This ring contains N, **Prefix is aza**
- The ring is 3-membered and fully saturated, **suffix is iridine**
- By combining the prefix and suffix, two vowels ended up together (aza~~iridine~~), therefore the vowel on the end of the first part should be dropped.
- This gives the correct name: Aziridine



Hantzsch-Widman RULE

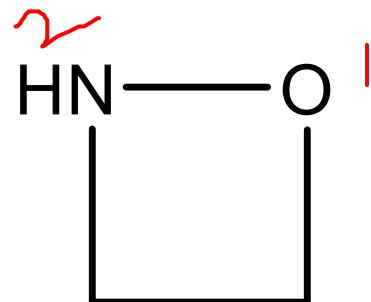


For example,

- This ring contains O, prefix 1 (oxa), and two N prefix 2 (diaza) ✓
- Locants, since (O) is higher priority than (N) so it is in position 1 by default and the two (N) are therefore at positions 2 and 5, this gives the combined prefixes as 1,2,5-oxadiaza (note that the a in oxa is not dropped) ✓
- It is 5-membered,fully unsaturated ring with (N) the suffix is ole ✓
- By combining the prefixes and the suffix and dropping the appropriate vowels we get the correct name as 1,2,5-Oxadiazole ✓



Hantzsch-Widman RULE

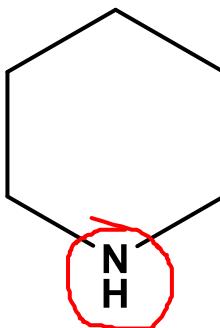


For example,

- This ring contains O, N and O has higher priority than N and by Prefix is 1,2-Oxaaza,
- But the starting numbering the ring at O first vowel must be omitted to give 1,2-Oxaza
- The ring is 4-membered and fully saturated, suffix is etidine
- By combining the prefix and suffix, two vowels ended up together 1,2 oaxazaetidine, therefore the vowel on the end of the first part should be dropped.
- This gives the correct name: 1,2-oxazetidine



Hantzsch-Widman RULE



For example,

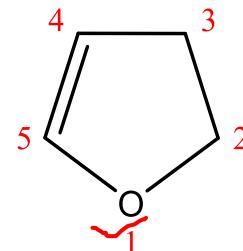
- The ring is 6-memberd, fully saturated with N, Prefix perhydro
- followed by the name of fully unsaturated 6-memberd ring with nitrogen azine
- Thus the full name is perhydroazine



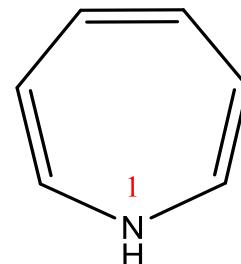
Hantzsch -Widman for partially unsaturated heterocycles

Partial unsaturation in heterocyclic compounds can be indicated by one of the following methods:

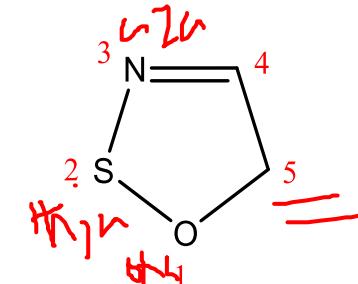
- ✓ The position of nitrogen or carbon atoms which bear extra hydrogen atoms must be indicated by numbers and italic capital H (e.g. 1H, 2H, etc.) followed by the name of maximally unsaturated ring.



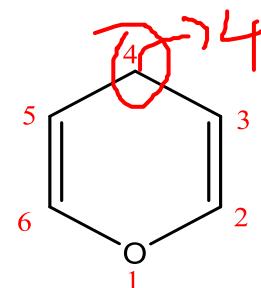
2H,3H-Oxole



1H-Azepine



5H,1,2,3-Oxathiazole

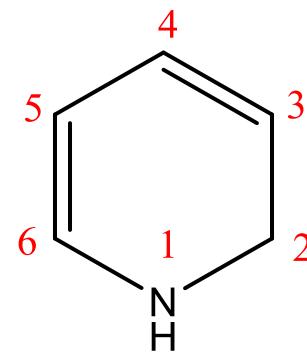


4H-Oxin

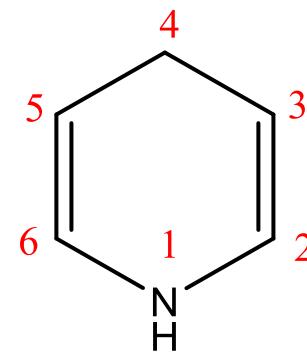


Hantzsch -Widman for partially unsaturated heterocycles

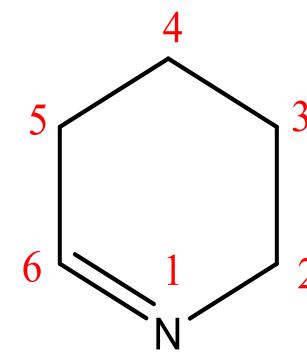
- ✓ The words **dihydro**, **trihydro** or **tetrahydro** are used if two or three or four atoms are saturated. These words are preceded by numbers indicate the position of saturated atoms as low as possible and followed by the corresponding fully unsaturated Hantzsch-Widman name.



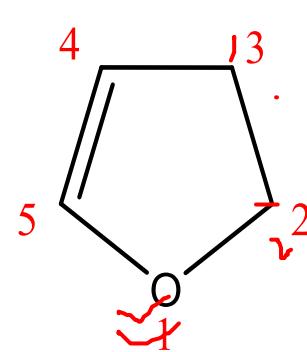
1,2-Dihydroazine



1,4-Dihydroazine



2,3,4,5-Tetrahydroazine



2,3-Dihydroxole



Hantzsch - Widman for partially unsaturated heterocycles

Alternatively, the partially unsaturated 4 and 5 rings (i.e. rings contain one double bond) are given special Hantzsch - Widman suffixes as in table and the double bond is specified as Δ^1 , Δ^2 , Δ^3 , etc.. Which indicates 1 and 2; 2 and 3; 3 and 4 atoms respectively have a double bond

Name : Δ^x + Prefix + special suffix

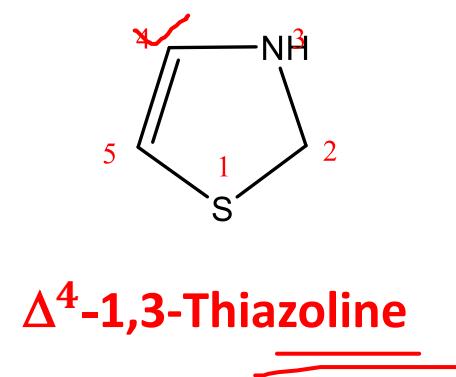
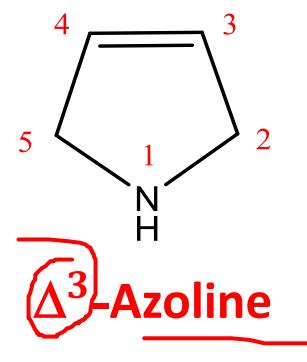
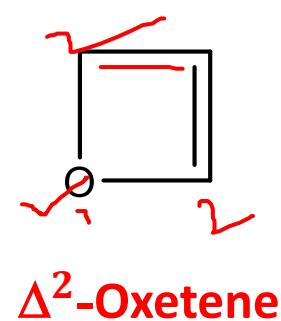
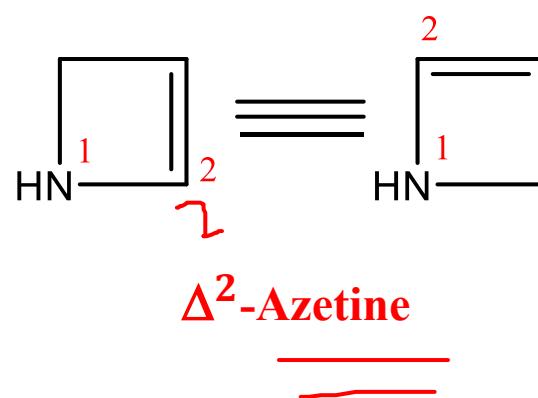
x= locant of the double bond

Ring Size	N Present	N Absent
4	-etine	-etene
5	-oline	-olene



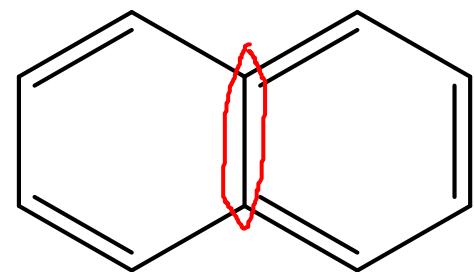
Hantzsch -Widman for partially unsaturated heterocycles

For example,



Heterocyclic Nomenclature of Fused Systems

- ✓ **Fusion:** This term is used to describe the process of joining two separate rings with the maximum number of non-cumulative double bonds via two atoms and one common bond.
- ✓ **Ortho-fused rings:** are those rings that have only two common atoms and one bond, example; naphthalene
- ✓ **Ortho-and peri-fused rings:** are those found in a polycyclic compound with a ring that is ortho- fused to different sides of two other rings that are themselves ortho-fused together (i.e. there are three common atoms between the first ring and the other two).

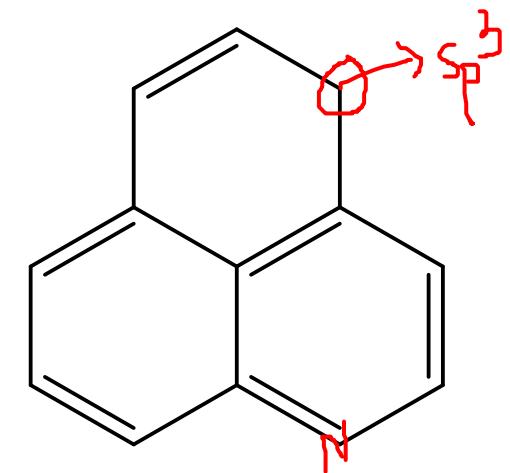


Naphthalene



Nomenclature of Fused Systems

- ✓ **1H-phenalene** is considered as being composed of three benzene rings, each is ortho-peri-fused to the other two.
- ✓ Polycyclic compounds incorporating one heterocyclic ring or fused heterocyclic system fused to benzene are known benzoheterocycles
- ✓ Also bicyclic compounds with two fused heterocyclic rings are well known.
- ✓ Both types can be named according to certain rules



1 H-Phenalene



Heterocyclic Nomenclature of Fused Systems

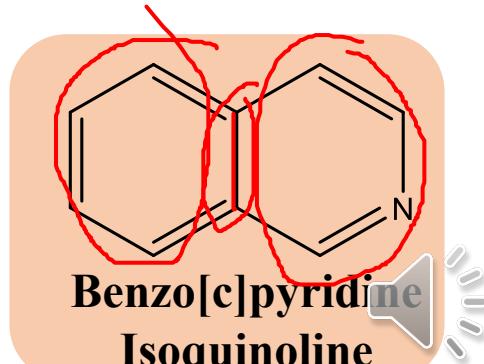
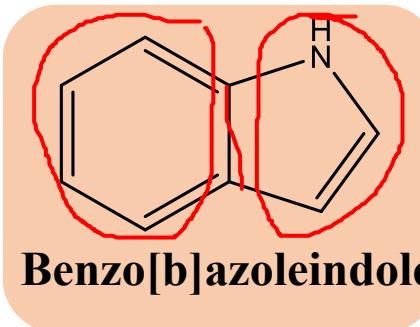
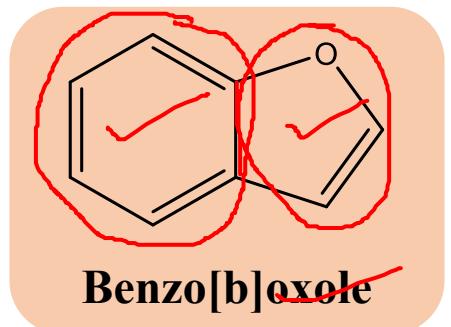
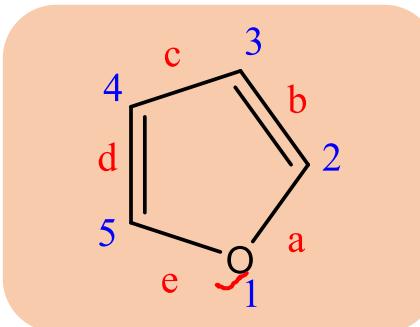
Nomenclature of benzofused compound

Polycyclic compounds incorporating one heterocyclic ring or fused heterocyclic system fused to benzene are known benzoheterocycles and is named by:

1. prefix: the word benzo
2. letter in square brackets: indicating the position of fusion
3. name of heterocyclic ring: common or IUPAC name.

Name= Benzo[letter]name of heterocyclic ring

(the connected bond take letter (a,b,c ...)



Heterocyclic Nomenclature of Fused Systems

Nomenclature of Fused Systems

- ✓ For designating the position of fusion the following rule is followed

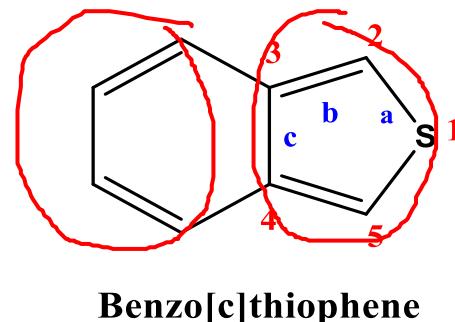
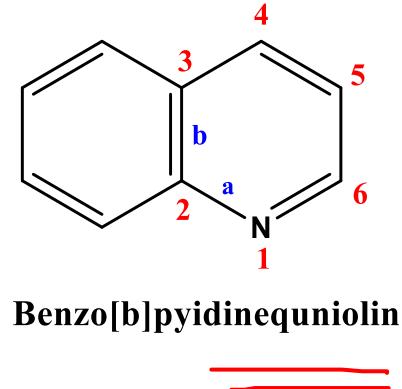
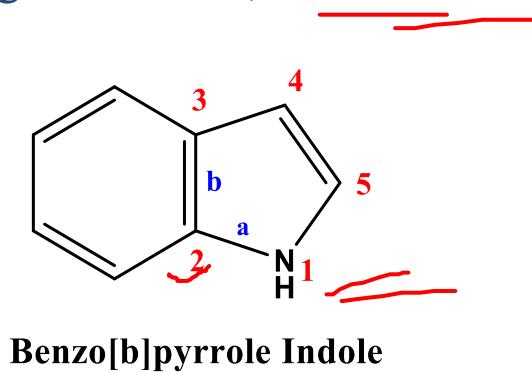
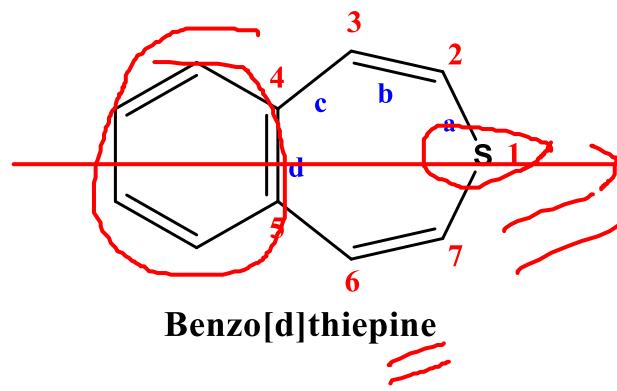
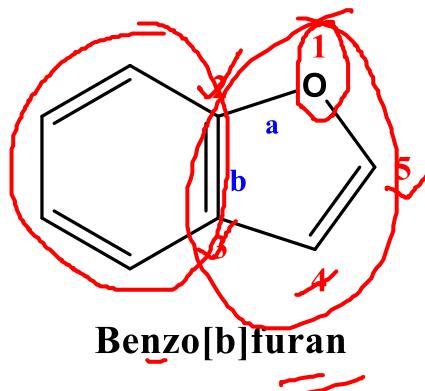
1. Numbering the H.C.R

- When numbering a ring with one heteroatom, the heteroatom is #1 and continues in the direction that is closer to the fused bond.
- When numbering a ring with more than one heteroatom, the highest priority atom is #1 and continues in the direction that gives the next priority atom the lowest number.



Heterocyclic Nomenclature of Fused Systems

2. The bonds of the heterocyclic ring are assigned by alphabetical letters starting with the 1,2-bond



Heterocyclic Nomenclature of Fused Systems

Nomenclature of fused heterocyclic compounds:

- ✓ Naming a fused heterocyclic systems composed of two mono heterocyclic units or benzoheterocycles (e.g. chromene) fused with another heterocycle ring is based upon considering one system as the parent (base) and the second is considered as substituent
- ✓ **The name is formed of : Name of substituent ring (minor ring)[number, number-letter]
name of base ring (major ring)**



Heterocyclic Nomenclature of Fused Systems

- ✓ The name of the minor ring is derived by writing a contracted prefix for the substituent ring present

Furo	From	Furan
Imidazo	From	Imidazole
Pyrido	From	Pyridine
Pyrimido	From	Pyrimidine
Thieno	From	Thiophene
Pyridazino	From	Pyridazine
Pyrazino	From	Pyrazine
Chromeno	From	Chromene



Heterocyclic Nomenclature of Fused Systems

- ✓ The no. indicate which atoms in the minor ring are common to the major ring (fusion sites in minor ring).
- ✓ The order of the numbers indicates which atom of the minor ring is encountered closest to atom 1 in the major numbering system (i.e. these numbers may be written in ascending or descending order e.g. 2,3 or 3,2)
- ✓ The letter defines the position of attachment of the minor ring to the major ring (fusion sites in base component)
- ✓ Finally a suffix indicate the name of the base ring is written.
- ✓ The numbering system for the whole fused system is not the same as the numbers in the square brackets (i.e. there are three numbering systems; one for minor ring, one for major ring and the third is for the system as a whole)



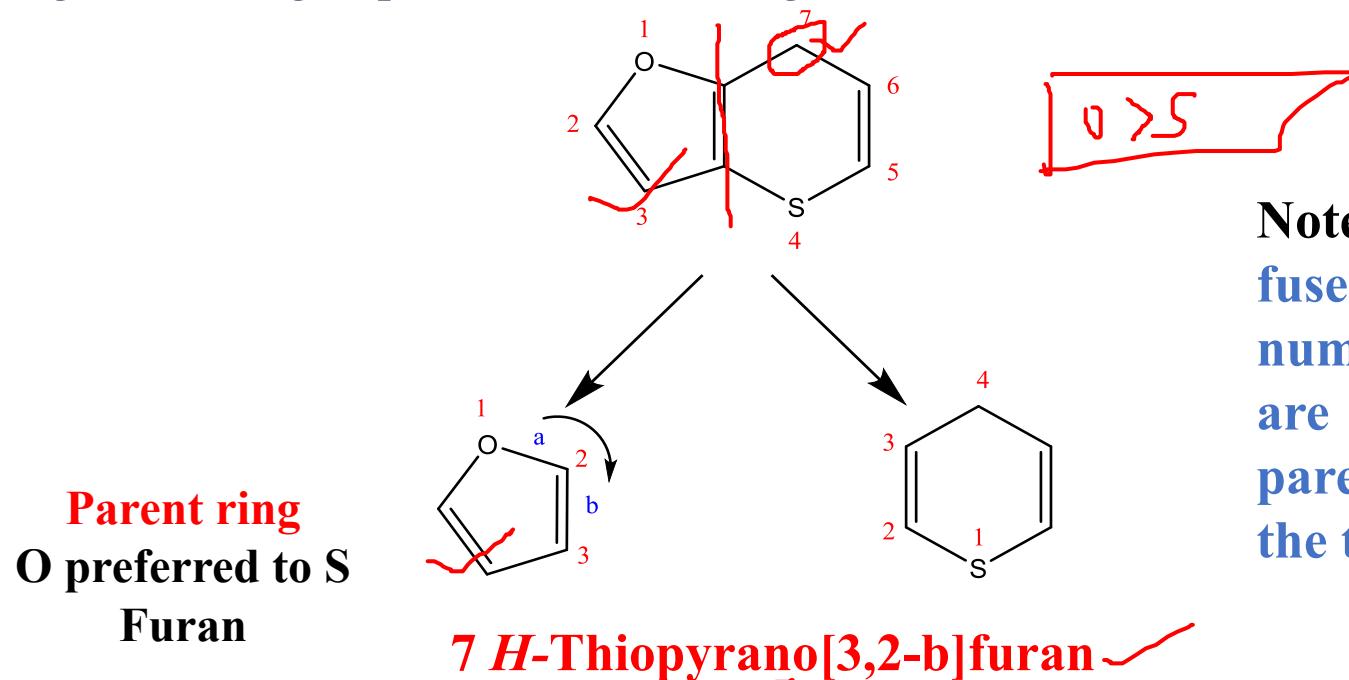
Heterocyclic Nomenclature of Fused Systems

- **Priority order of component ring systems:**

- ✓ Selection of a parent or base ring is based on the following rules which are applied in order

Rule 1: A heterocyclic ring containing the heteroatom occurring earliest in the order N, O, S

(i.e. ring containing N preferred to the rings does not contain N or containing O, or S)

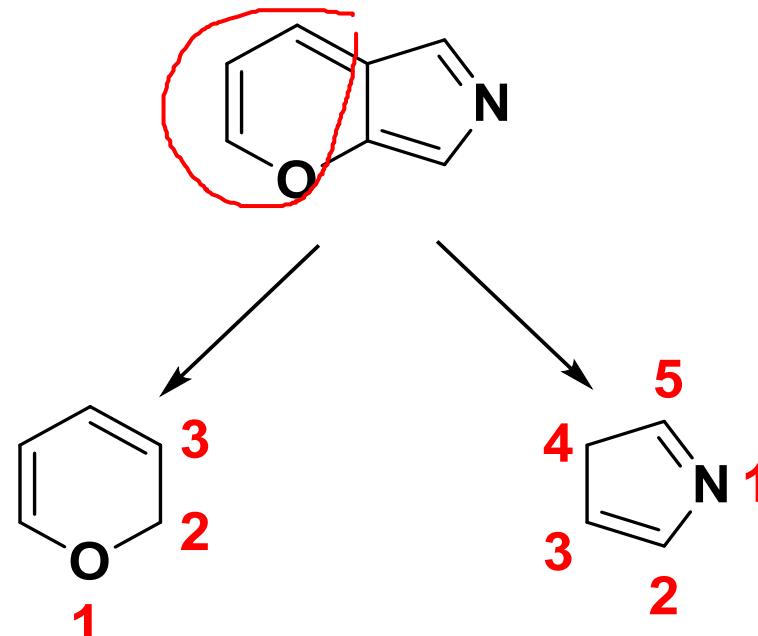


Note: The numbering system for the whole fused system is not the same as the numbers in the square brackets (i.e. there are three numbering systems; one for parent ring, one for substituent ring and the third is for the system as a whole)

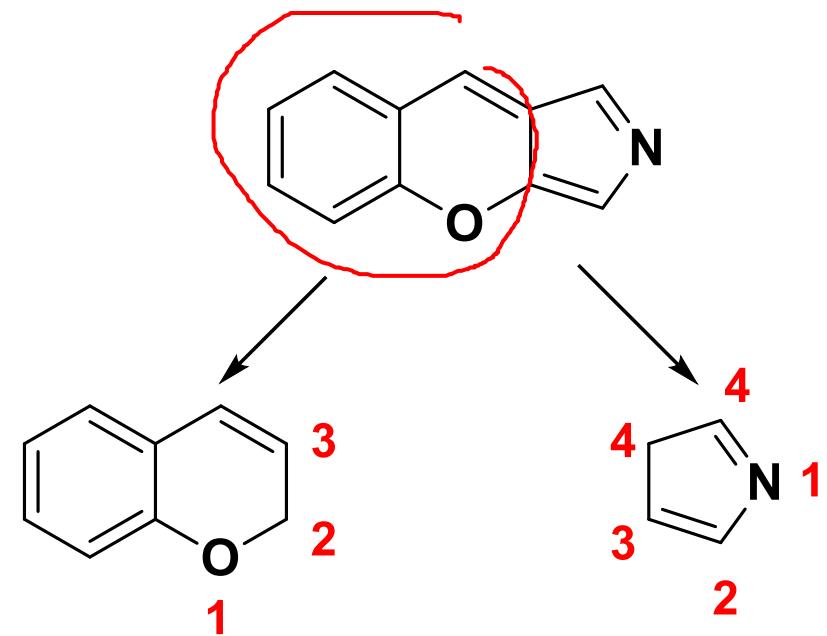


Heterocyclic Nomenclature of Fused Systems

- Priority order of component ring systems:



Pyrano[2,3-]pyrrole



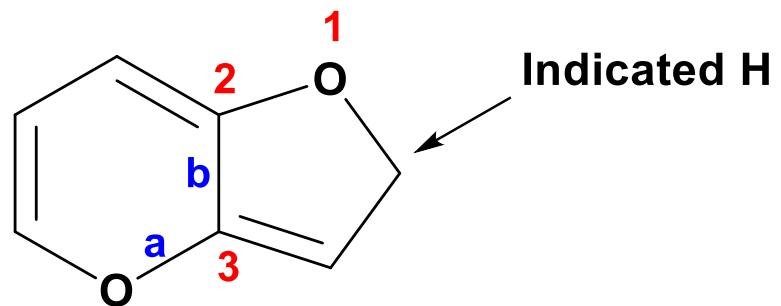
Chromeno[2,3-]pyrrole



Heterocyclic Nomenclature of Fused Systems

- Priority order of component ring systems:

Rule 2: A heterocyclic component containing the largest possible individual ring



**2H-Furo[3,2-b]pyran
(pyran [6] preferred to furan [5])**

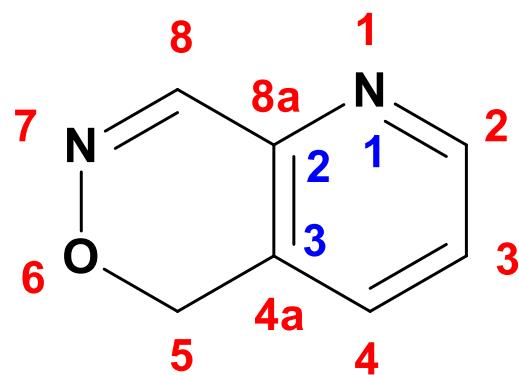
Note: Numbering the whole system is started from O in Furan ring to give the two hetero atom 1,4 while starting from O in pyran ring gives them 1,5 thus the indicated H takes 2



Heterocyclic Nomenclature of Fused Systems

- Priority order of component ring systems:

Rule 3: A heterocyclic component containing the greater number of heteroatom of any kind



**5H-Pyrido[2,3-d][1,2]oxazine
(Oxazine preferred to pyridine)**

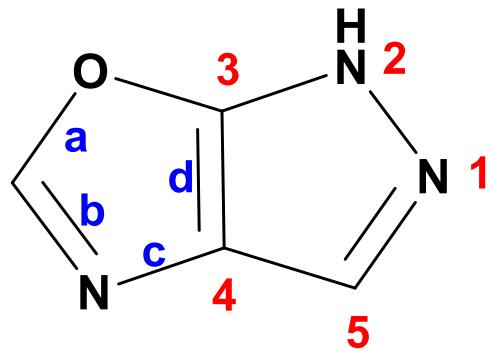
Note: The whole molecule is numbered starting from pyridine ring to give the three heteroatom the lowest possible number (1,6,7), however, stating from oxazine ring will give them (2,3,5) or (2,3,8).



Heterocyclic Nomenclature of Fused Systems

- Priority order of component ring systems:

Rule 4: A heterocyclic component containing the greater variety of heteroatom



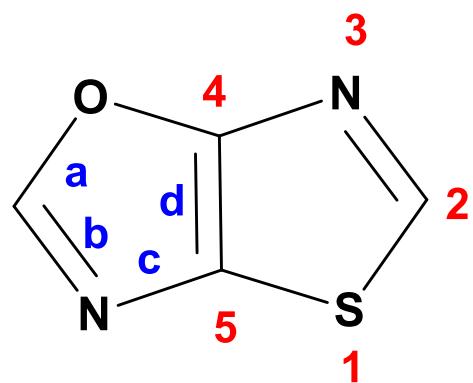
**1H-Pyrazolo[4,3-d]oxazole
(O & N preferred to N only)**

Note: The whole molecule is numbered starting from pyrazole ring to give the four heteroatom the lowest possible number (1,2,4,6). While starting from oxazole ring give them (1,3,4,5) or (1,3,5,6).

Heterocyclic Nomenclature of Fused Systems

- Priority order of component ring systems:

Rule 5: A heterocyclic component containing the greater number of heteroatoms most preferred when considered in order O, S,N,



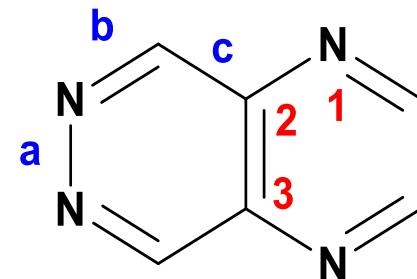
[1,3]Thiazolo[5,4-d][1,3]oxazole
(N & O preferred to N & S)

Heterocyclic Nomenclature of Fused Systems

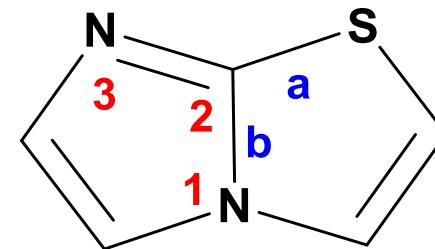
- **Priority order of component ring systems:**

Rule 6: A heterocyclic component with the lower possible number for heteroatoms

Rule 7: If a position of fusion is occupied by a heteroatom the name of the component rings to be used are so chosen as both to contain the heteroatom.



Pyrazino[2,3-d]pyridazine
(pyridazine [2N-1,2] preferred to pyrazine [2N-1,4])



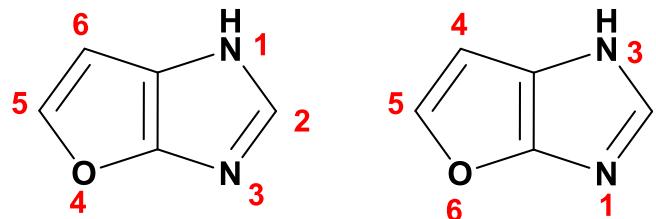
Imidazo[2,1-b]thiazole

Heterocyclic Nomenclature of Fused Systems

Order of preference between alternative numbering system of the whole molecule

Numbering the whole fused system should start from the first atom after fusion in any direction to fulfill the following rules in order:

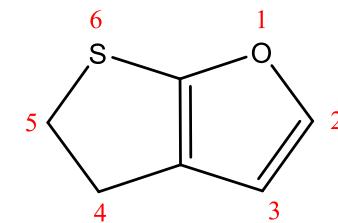
a) Give low numbers for the heteroatoms as a set



1H-Furo[2,3-d]imidazole

(heteroatoms 1,3,4 is preferred to 1,3,6 or 1,4,6)

b) Give low numbers for heteroatoms of higher priority O,S, N



4,5-Dihydro-thieno[2,3-b]furan

THANK YOU