NOMENCLATURE OF FUSED RING HETEROCYCLES
Fused heterocycles are systems constructed by combining two or more rings.

The rings are fused if they are linked in such a way that each ring has one common bond (fusion bond) to each other.

Moreover, each of the fused ring units should contain a maximum number of non-cumulative double bonds.

There are two broad types of fused heterocycles. They involve either a aromatic carbocycle linked to a heterocycle or a heterocycle linked to another heterocycle.
Hantzsch-Widman Nomenclature
Rules for Naming Fused Heterocycles

• Many of these fused heterocycles occur naturally in plant and animal systems, and some are used commercially.
• Due to their traditional uses, some of these heterocycles have trivial names that reflect these uses, but also have IUPAC names that reflect their structure.
• The general format for the name of a fused heterocycle involving a carbocycle fused to a heterocycle is:

\[
\text{Name of fused heterocycle} = \text{Prefix} + [\text{alphabet}] + \text{Suffix} \\
\triangle \quad \triangle \quad \triangle \\
\text{Attached component} \quad \text{Fusion bond} \quad \text{Base component}
\]

• To generate this name, it is necessary to identify the fused or attached ring and the base ring that will be the parent ring that will provide the suffix of the molecule.
Hantzsch-Widman Nomenclature
Rules for Naming Fused Heterocycles

• To derive the name of the fused heterocycle, the attached component is added as a prefix to the name of the base component.
• The prefix in such names is generated by replacing the terminal ‘e’ in the name of the attached component by ‘o’, i.e. benzo, naphtho and so on.
• The prefixes for the common aromatic heterocycles are listed below:
  ✓ Furan = furo
  ✓ Thiophene = thieno
  ✓ Pyridine = pyrido
  ✓ Pyrrole = pyrrolo
  ✓ Imidazole =imidazo
  ✓ Quinoline = quino
Hantzsch-Widman Nomenclature
Identifying the Fused Components

• To identify the fused components of a fused heterocycle, dissect it along the fusion bond into its component rings to set one as its base component and the other will be designated as the attached component.

• Note that the base component is always a heterocyclic system. The components are given their recognized trivial names (if possible) else, systematic name is used.
Hantzsch-Widman Nomenclature
Naming a Carbocycle Fused to Heterocycle

- To name a fused heterocycle, derived from the fusion of a carbocycle to a heterocycle:
  i. Derive the parent name (written at the end) from the name of the heterocyclic ring (base component).
  ii. Generate the attached name (written first) from the name of the attached benzene (i.e. Benzo).
  iii. The bond of fusion of the parent ring with the attached benzene ring is indicated using alphabetical letters (a, b, c etc) placed in square brackets between the prefix and parent name.
  iv. To determine the alphabet for the bond of fusion, number the parent ring from the heteroatom to the fusion bond such that side 1,2, takes letter (a), side 2,3 takes letter (b), side 3, 4 takes letter (c) etc.
Hantzsch-Widman Nomenclature

Worked Example: Indole

• To nomenclature of indole illustrated below shows how fused heterocycles with a carbocycle fused to a heterocycle are named:

\[
\text{Parent name = Pyrrole} \\
\text{Prefix = Benzo} \\
\text{Fusion side = } [b] \\
\text{Full name = Benzo}[b]\text{pyrrole} \\
\text{(Trivial name = Indole)}
\]
Hantzsch-Widman Nomenclature
Carbocycle Fused to Heterocycle

• Following a similar approach, verify that the fused heterocycles below are named as follows:

- Benzo[b]pyridine (Quinoline)
- Benzo[c]pyridine (Isoquinoline)
- 4,5-Dihydrobenzo[c]thiophene

• Note that when the fused heterocycles are partially saturated or substituted, the total numbering of the complete fused system is done to determine the positions of saturations or substitutions.

• The numbering starts from the atom next to the fusion point giving the heteroatom the least possible locant and the fused bond is given the fusion number using letters (a, b, c, etc).
Hantzsch-Widman Nomenclature
Heterocycle Fused to Another Heterocycle

• The IUPAC nomenclature of such systems is based on:
  i. The parent name (suffix) of the base component is given by the higher priority heterocycle.
  ii. The attached component is the ring name of the lower priority ring and is used as the prefix.
• The bond of fusion is indicated by numbers and an appropriate letter enclosed in a square bracket and placed immediately after the prefix.
• The numbers (positions of attachment) of the attached component are placed in the sequence in which they are attached to the base component.
• For substituted systems, the total numbering of the fused heterocycle is in the usual way 1,2,3….based on the principle of lowest possible numbering.
Hantzsch-Widman Nomenclature
Heterocycle Fused to Another Heterocycle

- The general format for capturing the name of a fused heterocycle combining a heterocycle fused to another heterocycle is summarized below:
  i. The parent or base name given by the higher priority heterocycle is used as suffix.
  ii. The fused ring name is the lower priority ring and is used as prefix.

```
Name of fused heterocycle
  ▼
Prefix + [ numbers + alphabet] + Suffix
  ▲
Attached component          Fusion bond          Base component
  ▲ Lower priority heterocycle          Higher priority heterocycle
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Hantzsch-Widman Nomenclature
Rules for Fused Aromatic Heterocycles

- If there is a choice between different heterocyclic components, nitrogen-containing components take singular precedence over all other heterocycles as the base component.

- If nitrogen is absent, then the ring with other heteroatom(s) is selected as base component based on the order of preference (oxygen > sulphur).
Hantzsch-Widman Nomenclature

Rules for Fused Aromatic Heterocycles

• If components have the same heteroatom, but rings of unequal size are present, then the one with largest size of the ring is selected.

\[ \text{Fused heterocycle} \quad \Rightarrow \quad \text{Base component} = \text{Pyran} \]

• If rings of equal size with different number of heteroatoms are present, then the ring with greater number of heteroatoms of any kind is considered as a base component.

\[ \text{Fused heterocycle} \quad \Rightarrow \quad \text{Base component} = \text{Oxazole} \]
Illustrated below is the process of naming a fused heterocycle combining a heterocycle fused to another heterocycle.

**Base component**
- Parent name = Pyrrole
- Prefix = Furo
- Fusion point = [2.3-b]

**Attached component**
- Fusion bond number

**Fusion bond letter**
- 6H-furo[2,3-b]pyrrole
Note in these examples that the number for the obligatory saturated carbon is determined by the numbering that gives the two heteroatoms the lowest combination of location numbers.

**5-Methyl-2H-furo[3,2-b]pyran**  
Base component = Pyran

**5-Methyl-5H-furo[3,2-b]pyran**  
Base component = Pyran
Hantzsch-Widman Nomenclature

Fused Heterocycles with Polyheteroatoms

• For fused heterocycles containing a heterocycle with a multiplicity of heteroatoms, the ring containing the greatest number of heteroatoms or greatest varieties of heteroatoms is the parent ring.

![Pyrido[2,3-d]pyrimidine](image1) 4H-Pyrrolo[3,2-d]oxazole 6H-Imidazo[4,5-d]thiazole

• The peripheral numbering of the total heterocyclic fused molecule is by giving the lowest number to the higher priority heteroatom especially when present just after fusion. But, if the more prior heteroatom is not the nearest to the fusion side the other nearest heteroatoms after fusion must take the least possible numbering regardless of priority.
Hantzsch-Widman Nomenclature
Fused Heterocycles with Multiple Heteroatoms

- For fused heterocycles containing a heterocycle with a similar number and type of heteroatoms, the ring containing the greater number of carbon atoms adjacent to the bond of fusion is the parent ring.
Provide the IUPAC names of the following fused heterocycles.