A selection of the structures, names and standard numbering of the more common heteroaromatic systems and some common non-aromatic heterocycles, are shown in this chapter. The aromatic heterocycles are grouped into those with six-membered rings and those with five-membered rings. The names of six-membered aromatic heterocycles that contain nitrogen generally end in ‘ine’, though note that ‘purine’ is the name for a very important bicyclic system which, has both a six- and a five-membered nitrogen-containing heterocycle. Five-membered heterocycles containing nitrogen generally end with ‘ole’. Note the use of italic ‘\( H \)’ in a name such as ‘\( 9H \)-purine’ to designate the location of an \( N \)-hydrogen in a system in which, by tautomerism, the hydrogen could reside on another nitrogen (e.g. N-7 in the case of purine). Names such as ‘pyridine’, ‘pyrrole’ and ‘thiophene’ are the original, and now standard, names for these heterocycles; names such as ‘1,2,4-triazine’ for a six-membered ring with three nitrogens located as indicated by the numbers, are more logically systematic.

A detailed discussion of the systematic rules for naming polycyclic systems in which several aromatic or heteroaromatic rings are fused together, is beyond the scope of this book, however, two simple examples will serve to illustrate the principles. In the name ‘pyrrolo[2,3-\( b \)]pyridine’, the numbers signify the positions of the first named heterocycle, numbered as if it were a separate entity, which are the points of ring fusion; the italic letter, ‘\( b \)’ in this case, designates the side of the second named heterocycle to which the other ring is fused, the lettering deriving from the numbering of that heterocycle as a separate entity, that is, side \( a \) is between atoms 1 and 2, side \( b \) is that between atoms 2 and 3, and so on. Actually, this particular heterocycle is more often referred to as ‘7-azaindole’ – note the use of the prefix ‘aza’ to denote the replacement of a ring carbon by nitrogen. Similarly, ‘5-azaindole’ is systematically called ‘pyrrolo[3,2-\( c \)]pyridine’ – note that the order of the numbers ‘3,2-’ arises because the first atom of the pyrrole encountered in counting round from the pyridine nitrogen to determine the side of fusion, and thus the label ‘\( c \)’, is C-3 of the pyrrole unit.

The numbering of a bi- or polycyclic system as a whole is generated from a series of rules concerned with the orientation of the rings and the positions of the nitrogen(s), but we do not deal with these here – the overall numbering for these two systems is shown for two substituted examples.

A device that is useful in discussions of reactivity is the designation of positions as ‘\( \alpha \)’, ‘\( \beta \)’ or ‘\( \gamma \)’. For example, the 2- and the 6-positions in pyridine are equivalent in reactivity terms, so to make discussion of such reactivity clearer, each of these positions is referred to as an ‘\( \alpha \)-position’. Comparable use of \( \alpha \) and \( \beta \) is made in describing reactivity in five-membered systems. These useful designations are shown on some of the structures. Note that carbons at angular positions do not have a separate number but are designated using the number of the preceding atom followed by ‘\( a \)’ – as illustrated for quinoline.
Heterocyclic Nomenclature

Six-membered aromatic heterocycles

Five-membered aromatic heterocycles
Non-aromatic heterocycles

Small-ring heterocycles