Torsion angles play an important part in discussions of stereochemical problems and so the terminology relating to them must be precise as far as possible. While the different terms so far used such as eclipsed (opposed), gauche (skew), anti, and skewed are quite adequate for specifying the conformations of molecules when both the atoms flanking the bond are tetrahedral, some of the terms lose their significance in describing conformations where one or both the atoms are trigonal. The torsion angle is no longer a multiple of 60° but can have intermediate values. In fact, even for the tetrahedral compounds, in most cases the torsion angles are different from the idealised values. A general and detailed method of nomenclature has been worked out by Klyne and Prelog (1960) to describe steric relationship across a single bond in a molecule or part of a molecule. The rules are discussed below.

1. Torsion angle although used interchangeably with dihedral angle has a slightly different connotation. Thus while dihedral angle is the angle between two *planes* defined by A-X-Y and X-Y-B in molecules of the type A-X-Y-B, the torsion angle is the angle subtended by A and B *across* the bond X-Y. In contrast to dihedral angle, torsion angle has a directional property, (+) when measured in a clockwise direction and (–) when measured in an anticlockwise direction starting from the front substituent A and ending at the rear substituent B. It may be measured from 0° to 360° continuously following a clockwise direction but the general practice is to express it by the smaller angle prefixed by (+) or (–). In subsequent discussions, torsion angle (θ)* will be used most of the time.

2. For specifying torsion angle, it is necessary to specify two fiducial (reference) groups one from each set of substituents across the bond and this is done according to the Conformation Selection Rule (Cahn et al 1966) which are: (*i*) If all substituents in a set are different, the sequence rule preferred group is selected. (*ii*) If two in a set are identical, the non-identical group is chosen irrespective of the sequence rule. (*iii*) If all the substituents in a set are identical, that which makes the smallest torsion angle is chosen.

3. The fiducial group at the front atom is preferably placed at the top of the Newman projection formula and the torsion angle is described in terms of three pairs of self-explanatory designations: (*i*) (+) and (–) for a rotation of 0° to 180° in clockwise and anticlockwise directions respectively. (*ii*) syn for a value of 0° – 90° and anti for a value of 90°-180° in both directions; and (*iii*) periplanar meaning approximately planar and clinal meaning inclined. The conformations bear the designation of the torsion angle expressed within ± 30°. Six such combinations for *n*-butane type of molecules are possible and they are listed in Table 9.2 along with the current nomenclature. The sign of torsion angle in any conformation remains unchanged whether the molecule is viewed from the front or from the rear; in the first case, it is measured from A to B and in the second, from B to A, A and B being the two fiducial groups.

*D...

Table 9.2 Designations of conformations based on torsion angle

Torsion angle (θ)	Designation	Symbol	Reference to *n*-butane	θ as a multiple of 60°
0° ± 30°	± syn-periplanar	± *sp*	eclipsed (I)	0
+ 60° ± 30°	+ syn-clinal	+ *sc*	gauche (II), P	1
+ 120° ± 30°	+ anti-clinal	+ *ac*	eclipsed (III)	2
180° ± 30°	± anti-periplanar	± *ap*	anti (IV)	3
− 120° ± 30°	− anti-clinal	− *ac*	eclipsed (V)	4
− 60° ± 30°	− syn-clinal	− *sc*	gauche (VI), M	5

The advantages of this system are: The torsion angles are expressed within a range, which is more realistic since often their exact values are not known; the (+) and (–) signs immediately show the direction of a torsion angle; it is applicable to any molecule or a part of a molecule typified by a segment A-X-Y-B whether X and Y are tetrahedral or other than tetrahedral; and finally, it may be used with advantage to describe partial conformation of polymer chains and ring compounds. A few illustrations of different types are given in Figure 9.4.

meso-1, 2-Dichloro-1, 2-diphenylethane (stilbene dichloride) exists in three conformers (VII*a*), (VII*b*), and (VII*c*) (Figure 9.4*a*) which have torsion angles of 180°, – 60°, and + 60° (the fiducial groups are the Cl atoms) and are designated (±) *ap*, (–) *sc*, and (+) *sc* respectively. Of the three, (±) *ap* is the most stable conformer, the bulky phenyl groups being anti (see discussion on dipole moment). Similarly, the (1S, 2S) enantiomer of the optically active form exists in three conformers (VIII*a*), (VIII*b*), and (VIII*c*) which are designated (–) *sc*, (+) *sc* and (±) *ap* respectively. Here probably the conformer (VIII*b*) is more stable (see Eliel and Brunet 1986 for conformational analysis of stilbene dibromides).

Propionaldehyde is an example in which the rotation to be considered is around an sp^3-sp^2 bond. It exists in three conformations in each of which either H or Me is eclipsed with the C = O bond*. The fiducial groups are oxygen and Me and the designations of the three conformers (Figure 9.4*b*) from left to right are respectively (±) *sp*, (+) *ac*, and (–) *ac* with torsion angles of 0°, + 120°, and –120° approximately.

Polypropylene forms two types of linear chains, syndiotactic in which the consecutive chiral centres have opposite chirality and isotactic in which they have the same chirality.† The former exists layered in an all antiperiplanar conformation (IX, Figure 9.4*c*), represented by $(\pm\ ap)_n$ or $(180°)_n$ the antiperiplanar conformation (X) incurs severe non-bonded interactions among the syn methyl groups

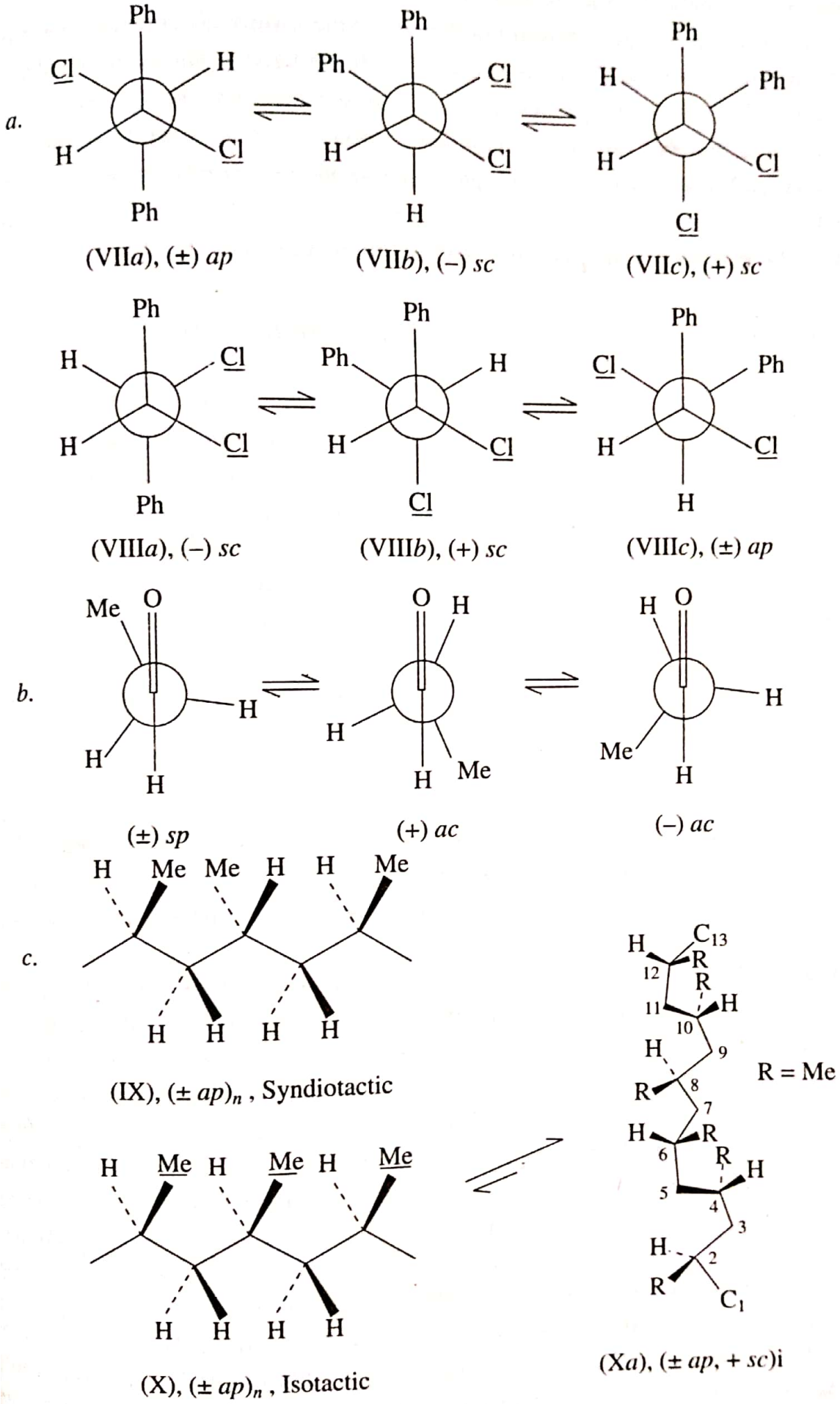

Figure 9.4 Klyne-Prelog nomenclature for torsion angles

which is avoided by assuming a helical conformation in which the torsion angles alternate between 180° and + 60° or 180° and – 60° as one proceeds along the chain; the former arrangement constitutes an M helix and the latter a P helix. An approximate diagram of the M helix is shown in the structure (X*a*) which may be designated $(180°, + 60°)_n$ or $(\pm\ ap, + sc)_n$. In the diagram, the torsion angles are successively 180° (around C_2-C_3), + 60° (around C_3-C_4), 180° (around C_4-C_5), + 60° (around C_5-C_6), and so on. C_7 is the translational repeat of C_1, C_8 of C_2 etc., three monomeric units making a complete 360° turn (Goodman 1967).