

this chapter.

## 1.5 Rotation around bonds and change in dihedral angle

It has previously been noted that rotation about a single bond (e.g., C—C) is relatively free while rotation around a double bond (e.g., C=C) is highly restricted. Between these two extremes, there exist also intermediate bonds with fractional bond order arising out of internuclear delocalisation of electrons. Rotation around these bonds are also more or less restricted. These three types of bonds are discussed in the context of restricted rotation and change of dihedral angle.

### 1.5.1 Rotation around a single bond

According to the *principle of free rotation* of classical stereochemistry, rotation around a single bond was considered to be free. Strictly speaking, this would mean that the potential energy of the molecule is independent of the dihedral angle. However, calculation of enthalpy and entropy of ethane based on statistical mechanics showed that in order to bring agreement between the calculated and experimental values, an energy barrier of  $12.5 \text{ kJ mol}^{-1}$  has to be assumed. The diagram (Figure 1.5) shows the change of enthalpy with the change of dihedral angle from  $0^\circ$  to  $360^\circ$ . Three energy minimum conformations\*, known as conformers and three energy maximum conformations representing the energy barrier arise during the operation. For ethane, the three conformers are equivalent as are the three energy maxima (barriers to rotation).

In order to specify the conformations, it is necessary to represent them in perspective formulae following certain conventions. Three modes of representations are commonly used, namely, sawhorse formula, Newman projection formula, and flying wedge formula (see Chapter 3). The first two are illustrated by the structures (XVIII) and (XIX) (for ethane) respectively. In sawhorse formula, the C—C bond is viewed sideways while in Newman projection formula, the C—C bond lies

\*Spatial orientations of a molecule which differ only in the dihedral angle and are easily interconvertible are called conformations. More detailed definition is given in Chapter 10.

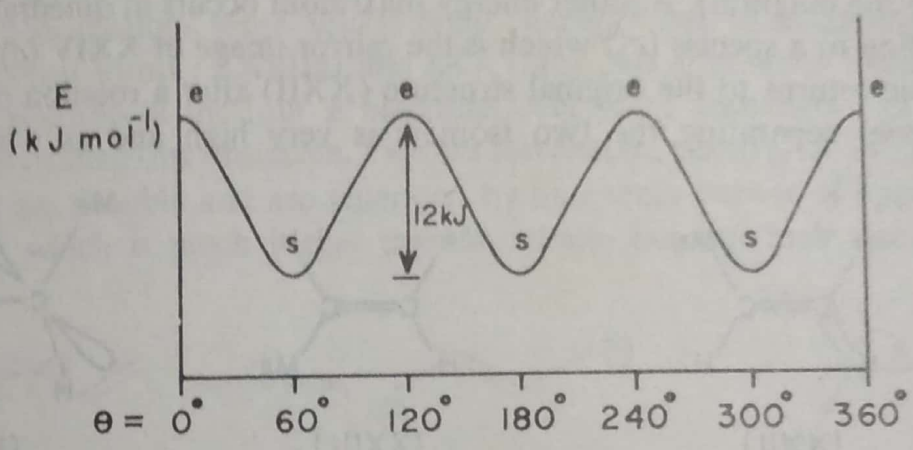
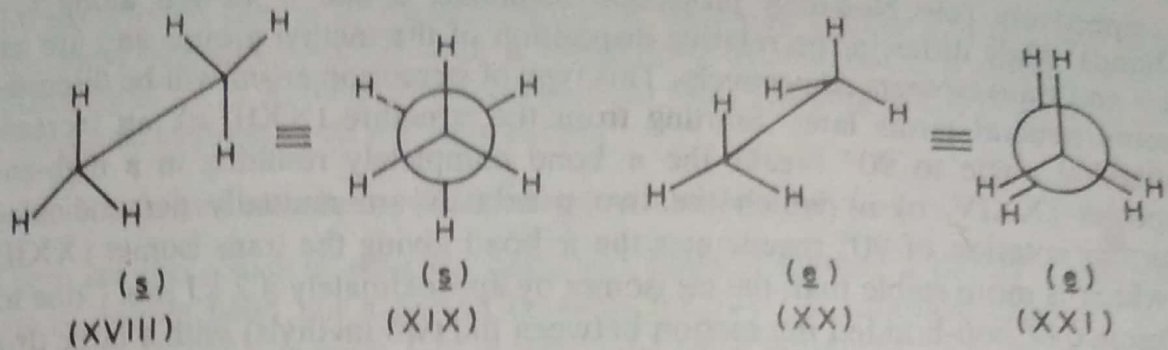


Figure 1.5 Restricted rotation in ethane

along the line of vision and cannot be seen. The other bonds are oriented radially making  $120^\circ$  angle with one another. The  $109.5^\circ$  angle of a tetrahedral carbon and  $120^\circ$  angle of a trigonal carbon would appear as  $120^\circ$  and  $180^\circ$  respectively when projected on a plane. The conformation (XVIII) or (XIX) with the six hydrogen atoms positioned as far apart as possible is called staggered (s). The conformation (XX) or (XXI) with the hydrogen atoms in pairwise conjunction is called eclipsed (e). The dihedral angles are respectively  $60^\circ$  and  $0^\circ$  in these two conformations. A detailed nomenclature will be given elsewhere.

According to the spectral evidence, the staggered conformations are energetically preferred and contribute to the ground state population of ethane. The eclipsed conformations correspond to the energy maxima in the diagram and serve as barriers between the conformers. Since the energy barrier is low ( $12.5 \text{ kJ mol}^{-1}$ ), the interconversion of conformers in ethane is fast even at a comparatively low temperature, i.e., their kinetic stability is very low.

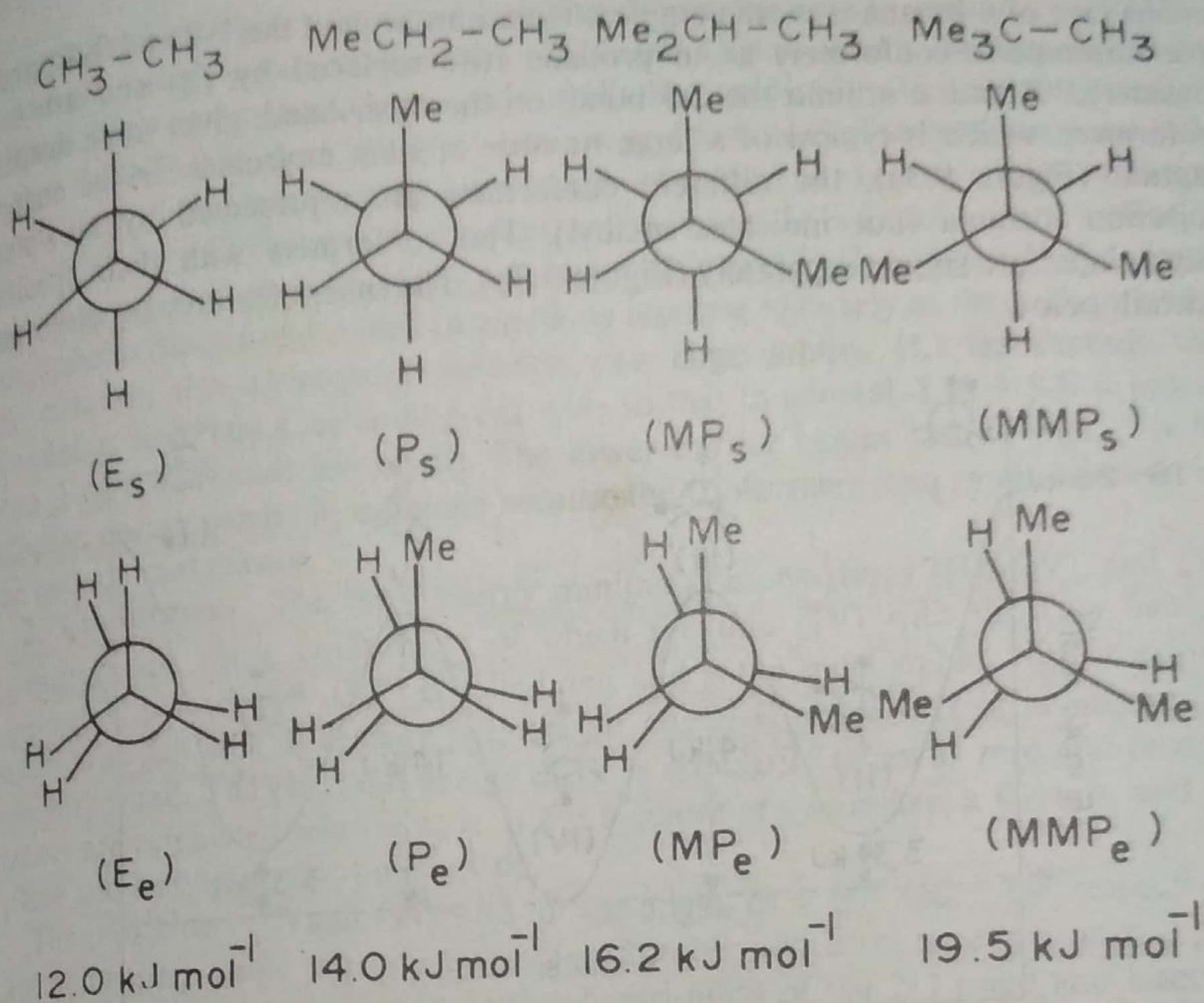
The torsional strain in the eclipsed ethane is believed to originate from the interaction of the eclipsed C—H bonds. Steric contribution due to non-bonded interaction between the vicinal hydrogens is negligible since the internuclear distance ( $0.23 \text{ nm}$ ) is almost equal to twice the value of van der Waals atomic radius of hydrogen ( $0.12 \text{ nm}$ ) (see Chapter 9).

### 1.5.2 Rotation around a double bond

Rotation around a double bond is highly restricted because it disrupts a  $\pi$  bond. 2-Butene can be represented by two isomeric structures (XXII) and (XXIII) (Figure 1.6), both being planar and having dihedral angles of  $0^\circ$  and  $180^\circ$

### 9.2.2 Conformation of ethane, propane, and *n*-butane

The potential energy diagram of ethane has already been depicted in Chapter 1. There are three equivalent energy minima corresponding to the staggered conformations ( $E_s$ ) and three equivalent energy maxima corresponding to the eclipsed conformation ( $E_e$ ) (Figure 9.2) with torsion angles  $60^\circ$ ,  $180^\circ$ ,  $-60^\circ$  and  $0^\circ$ ,  $120^\circ$ ,  $-120^\circ$  (with respect to a fixed pair of H's at C-1 and C-2) respectively. The important cases are those in which rotation around a single bond gives rise to three (as in the case of alkanes) or two (as in the case of biphenyls) or six (as in toluene or nitromethane or acetaldehyde) energy minima (Cahn et al 1966).



**Figure 9.2** Conformations of ethane, propane, 2-methylpropane, and 2,2-dimethylpropane

The energy barrier in ethane is  $12.0\text{--}12.5 \text{ kJ mol}^{-1}$ , approximately  $4 \text{ kJ mol}^{-1}$  per H-H eclipsing and has been said to be due to torsional (Pitzer) strain. For ethane, the distance between the pairs of eclipsed H's is  $0.23 \text{ nm}$  against the van der Waals atomic radii of  $0.24 \text{ nm}$ . The steric interaction in the eclipsing is thus trivial and at best accounts for only 10% of the total energy barrier. The origin of the major part of torsional strain is still controversial (may be due to an electronic factor). In the case of propane, the energy barrier, i.e., the difference in energies between the conformations  $P_e$  and  $P_s$  is  $14.0 \text{ kJ mol}^{-1}$ ,  $2.0 \text{ kJ mol}^{-1}$ , higher than that for ethane\*. Since the skew H-H and Me-H interactions (as in  $P_s$ ) are generally ignored, the value of  $2.0 \text{ kJ mol}^{-1}$  is attributed to a Me-H eclipsing.† In 2-methylpropane (isobutane), there are two such Me-H eclipsings and the energy barrier increases to  $16.2 \text{ kJ mol}^{-1}$ , (see  $MP_s$  and  $MP_e$ ) and in 2,2-dimethylpropane, there are three Me-H eclipsings and the energy barrier rises to  $19.5 \text{ kJ mol}^{-1}$ , (see  $MMP_s$  and  $MMP_e$ ). Thus for every Me-H eclipsing there appears to be a non-bonding interaction of approximately  $2.0 \text{ kJ mol}^{-1}$ .

The three conformers in each of the molecules differ by torsion angles of  $120^\circ$  among each other and are homomeric (periodicity = 3). In each set, they correspond to energy minima and are arbitrarily given zero potential energy.

\* E, P, MP, and MMP stand for ethane, propane, 2-methylpropane, and 2,2-dimethylpropane and s and e for staggered and eclipsed conformations respectively in Figure 9.2.

† This is in addition to the

The case of *n*-butane is more complex. Rotations around the 1-2 and 3-4 bonds give homomeric conformers as in propane (Me replaced by Et) and are not considered. Rotation around the 2-3 bond, on the other hand, gives three distinct conformers, which is typical of a large number of such molecules. In the energy diagram (Figure 9.3a), the different conformers are represented by Newman projection formula (dot indicates methyl). The conformers with their specific designations\* are shown separately (Figure 9.3b). The salient features are discussed in details below.

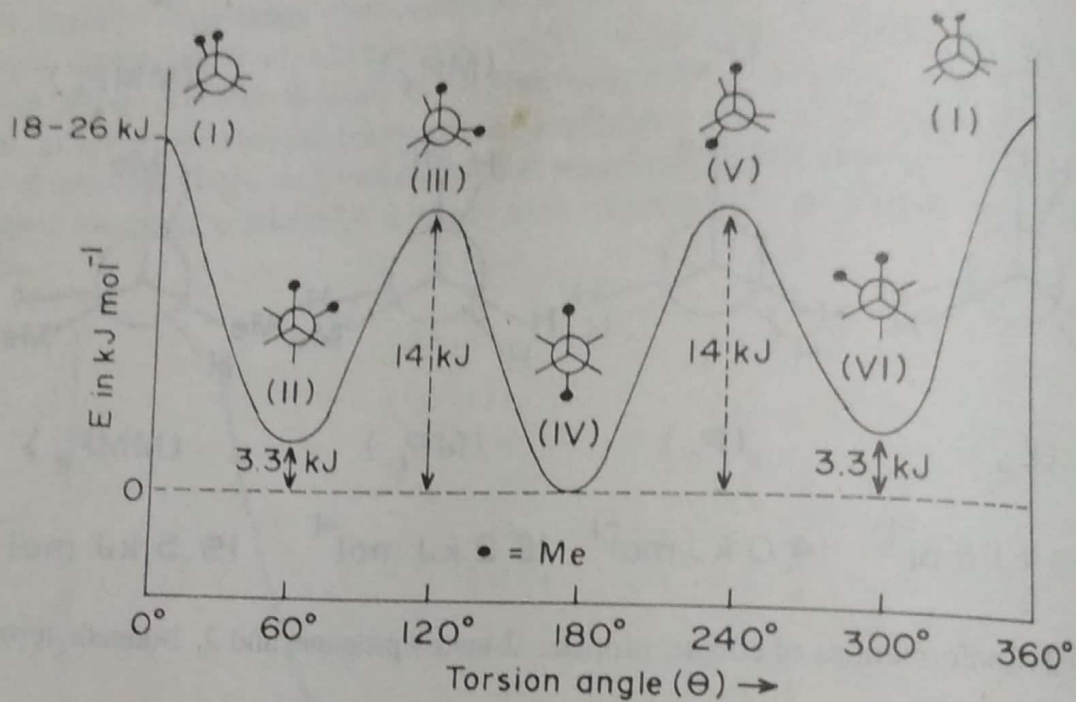
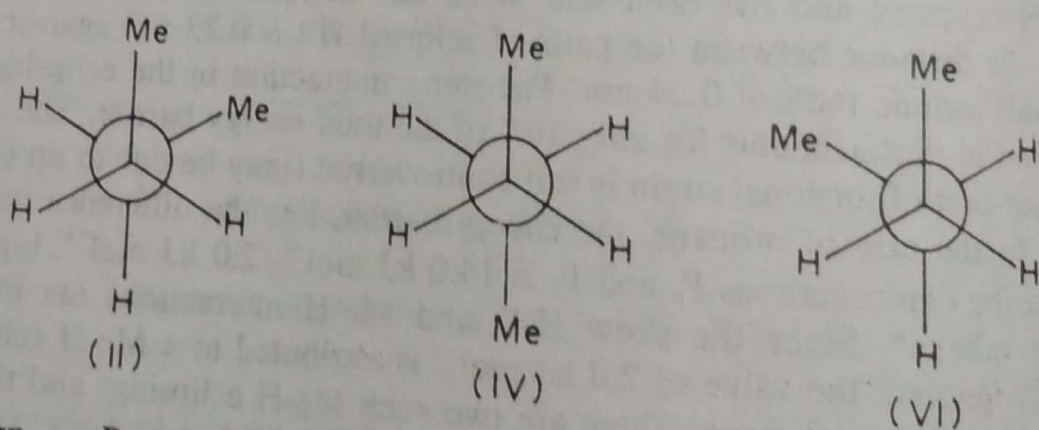


Figure 9.3a Potential energy diagram of *n*-butane



1. Desgn.	<i>P</i> - gauche (+) sc	anti (±) ap	<i>M</i> - gauche (-) sc
2. Symm.	$C_2$ point group $\sigma = 2$ $C_2$ axis	$C_{2h}$ point group $\sigma = 2$ $C_2$ axis, $\sigma$ plane	$C_2$ point group $\sigma = 2$ $C_2$ axis

Figure 9.3b Conformers of *n*-butane

Designation based on torsion angles is discussed later

1. Energy barriers : *n*-Butane exhibits a potential energy diagram with three maximum energy conformations (I), (III), and (V) of which the first with two eclipsed Me's and two pairs of eclipsed H's has predictably the highest potential energy, 18.0-26.0 kJ mol<sup>-1</sup>. It has a  $\sigma$  plane and is achiral. The conformations (III) and (V) are non-superposable mirror images of each other having torsion angles of + 120° and - 120° respectively with an energy of 14 kJ mol<sup>-1</sup>, very similar to that of an eclipsed propane. They contain a pair of Me-H and one H-H eclipsed interactions. Since non-bonded interactions increase inversely as the high power of the distance, the interactions between two large groups (L) far exceeds that between a large and a medium group (M) so that in general, L-L + S-S is greater than 2 M-S (S stands for small). The lower barrier height (14 kJ mol<sup>-1</sup>) is the effective energy barrier in *n*-butane because the conformers tend to interconvert via the path of least energy.

2. Conformers : The three energy minima conformations (II), (IV), and (VI) constitute the three conformers of which the one (IV) with the two methyls oppositely placed ( $\theta = 180^\circ$ ) is called *anti* and is the most stable. Here torsional strain is absent and, as already pointed out, the H-H and Me-H skew interactions are very small. The potential energy of IV is arbitrarily taken as zero and those of others are calculated relative to it. It has a centre of symmetry, a C<sub>2</sub> axis, and a  $\sigma$  plane and belongs to C<sub>2h</sub> point group.

The conformers (II) and (VI) with torsion angles of + 60° and - 60° respectively are non-superposable mirror images of each other and form an enantiomeric pair. They have a C<sub>2</sub> axis passing through the mid-point of the 2-3 bond and bisecting the dihedral angle between the two methyls and belong to C<sub>2</sub> point group. They are called *gauche* or *skew* conformers and their absolute configuration may be conveniently designated *P* and *M* in terms of helical chirality. They are equienergetic and have a potential energy of 3.3 kJ mol<sup>-1</sup> above that of IV which is commonly known as the *butane gauche* interaction\* and plays an important part in conformational analysis. In more general terms, the difference in potential energies between the most stable conformer of a molecule and a designated less stable one is called *conformational energy*. Since the torsional strain in *gauche* conformers is nearly zero, the *gauche* interaction originates from the non-bonded interaction between the two *gauche* methyls whose distance falls within the van der Waals group radii.

In general, the *gauche* interaction gets appreciable relief at the cost of some torsional strain by increase of the torsion angle by a few degrees. For example, electron diffraction experiments indicate a value of 63 ± 8° for the torsion angle in *gauche* butane. Wertz and Allinger (1974) put forward a hypothesis that while the non-bonded interactions between the *gauche* methyls can be minimised by a change of torsion angle and bond angle deformations, the H-H *gauche* interactions which are almost ubiquitous cannot generally be significantly reduced by any kind of molecular distortions and the origin of conformational energy both in acyclic

\*The best experimental values for butane *gauche* interaction appear to be 2.10-2.93 kJ mol<sup>-1</sup> in the liquid or solution phase and 3.68-4.2 kJ mol<sup>-1</sup> in the gas phase (Rosenthal et al 1982). A recently determined value from *trans*-1,2-dimethylcyclohexane (in liquid phase) is 3.10 ± 0.38 kJ mol<sup>-1</sup> (Manoharan and Eliel 1984).

and cyclic compounds might thus be traced to gauche H-H rather than gauche Me-Me interactions. The idea, however, did not gain any currency.

Any conformation intermediate between eclipsed and gauche is called *skewed* and its energy depends on its position on the potential energy diagram.

**3. Population of conformers:** The equilibrium population of any two conformers is given by the well known reaction isotherm (equation 6),

$$\Delta G^\circ = -RT \ln K \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (7)$$

where  $\Delta G^\circ$  is the free energy change in the standard state (Gibbs free energy) and is constant at a given temperature, and  $K$  (the equilibrium constant) expressed as the ratio of the more stable to the less stable conformers ( $\Delta G^\circ$  is thus negative). The standard free energy change is related to the enthalpy difference through an entropy term (equation 7). In many cases,  $\Delta S^\circ$  is small enough to be neglected, in which case the free energy change may be equated with the difference in enthalpy. In the present situation, however, the gauche conformers have a statistical advantage of 2, thus increasing the entropy by  $R \ln 2$  (which may also be ascribed to an entropy of mixing of two enantiomeric gauche forms). The free energy difference is thus reduced by  $RT \ln 2$  which at  $25^\circ\text{C}$  is  $1.7 \text{ kJ mol}^{-1}$  giving the value of  $1.6 \text{ kJ mol}^{-1}$  for  $\Delta G^\circ$  (with  $\Delta H^\circ = 3.3 \text{ kJ mol}^{-1}$ ). This corresponds to a population ratio of 1 : 2 for gauche and anti forms (the symmetry number for all the conformers is 2 and so is not taken into consideration). Accordingly, at room temperature, *n*-butane contains 66% of the anti (IV), 17% of *P*-gauche (II), and 17% of *M*-gauche (VI), the last two forming a racemic mixture.

As the temperature increases, the population of the less stable conformer increases and eventually becomes equal to that of the stabler conformer. On the other hand, at low temperature, the stable anti conformer prevails to a much greater extent and may become the only form detectable. At very low temperatures, the rate of interconversion is also very slow. If  $\Delta G^\circ$  exceeds  $10 \text{ kJ mol}^{-1}$ , the stabler isomer constitutes over 98% of the total at room temperature, ( $K = 49$ ) and such an equilibrium is called *anacomeric* (Antenius et al 1966) or conformationally biased and the molecule constitutes an anacomeric system (see Chapter 10) even though the rate of interconversion remains facile. Table 9.1 gives the conversion of a few conformational free energies into percentage populations of the stabler isomer using equation (6).

**Table 9.1** Conformational free energies and the populations of the stabler isomer at  $300 \text{ K}^a$

$\Delta G^\circ$		% of stabler isomer	$\Delta G^\circ$		% of stabler isomer
$\text{kJ mol}^{-1}$	$\text{kcal mol}^{-1}$		$\text{kJ mol}^{-1}$	$\text{kcal mol}^{-1}$	
0	0	50	3.4	0.82	80
0.5	0.12	55	4.3	1.03	85
1.0	0.24	60	5.5	1.30	90
1.5	0.37	65	7.3	1.74	95
2.1	0.50	70	9.6	2.31	98
2.7	0.65	75	11.4	2.72	99

<sup>a</sup>For data covering a wide range of temperature, see Gordon and Ford (1972).

4. **The shape of the diagram** : The variation of potential energy with torsion angle is approximately sinusoidal. Vibrational spectra as well as molecular mechanics calculations prove conclusively that the energy minima conformations correspond to the staggered forms and the energy maxima to the eclipsed forms. Since the non-bonded interactions increase very rapidly inside the eclipsed forms distance, it might have been expected that very sharp peaks would occur as the molecule rotates towards the eclipsed conformation bringing the atoms within contact distance. However, the process is also accompanied with deformations of bond angles having a soft energy function which take place in such a manner as to lower and round off the peaks. In any case, the high energy portions of the potential diagrams are rather poorly defined (Wilson 1972) and their nature remains obscure.

### 9.3 Klyne-Prelog terminology for torsion angles

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  $60^\circ$  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  $0^\circ$  to  $360^\circ$  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 ( $\theta$ )\* 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.

\*Dihedral angle is usually designated by the Greek letter theta ( $\theta$ ) whereas torsion angle is designated by various Greek letters, e.g.,  $\omega$  (omega),  $\phi$  (phi), and even  $\theta$ . IUPAC nomenclature (1974) recommends the use of  $\theta$  and  $\omega$  for torsion angle. In this text,  $\theta$  is used in most cases both for dihedral angle and for torsion angle where the sign of the angle is not important. For ring torsion angle, however,  $\phi$  is used following Bucourt (1974) where the signs of torsion angles are important.



(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  $0^\circ$  to  $180^\circ$  in clockwise and anticlockwise directions respectively; (ii) syn for a value of  $0^\circ$ - $90^\circ$  and anti for a value of  $90^\circ$ - $180^\circ$  in both directions; and (iii) periplanar meaning approximately planar and clinal meaning inclined. The conformations bear the designation of the torsion angle expressed within  $\pm 30^\circ$ . 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.

Table 9.2 Designations of conformations based on torsion angle

Torsion angle ( $\theta$ )	Designation	Symbol	Reference to <i>n</i> -butane	$\theta$ as a multiple of $60^\circ$
$0^\circ \pm 30^\circ$	$\pm$ syn-periplanar	$\pm$ sp	eclipsed (I)	0
$+ 60^\circ \pm 30^\circ$	+ syn-clinal	+ sc	gauche (II), P	1
$+ 120^\circ \pm 30^\circ$	+ anti-clinal	+ ac	eclipsed (III)	2
$180^\circ \pm 30^\circ$	$\pm$ anti-periplanar	$\pm$ ap	anti (IV)	3
$- 120^\circ \pm 30^\circ$	- anti-clinal	- ac	eclipsed (V)	4
$- 60^\circ \pm 30^\circ$	- 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 (VIIa), (VIIb), and (VIIc) (Figure 9.4a) which have torsion angles of  $180^\circ$ ,  $-60^\circ$ , and  $+60^\circ$  (the fiducial groups are the Cl atoms) and are designated ( $\pm$ ) ap, (-) sc, and (+) sc respectively. Of the three, ( $\pm$ ) ap is the most stable conformer, the bulky phenyl groups being anti (see discussion on dipole moment). Similarly, the (1*S*,2*S*) enantiomer of the optically active form exists in three conformers (VIIIa), (VIIIb), and (VIIIc) which are designated (-) sc, (+) sc and ( $\pm$ ) ap respectively. Here probably the conformer (VIIIb) 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

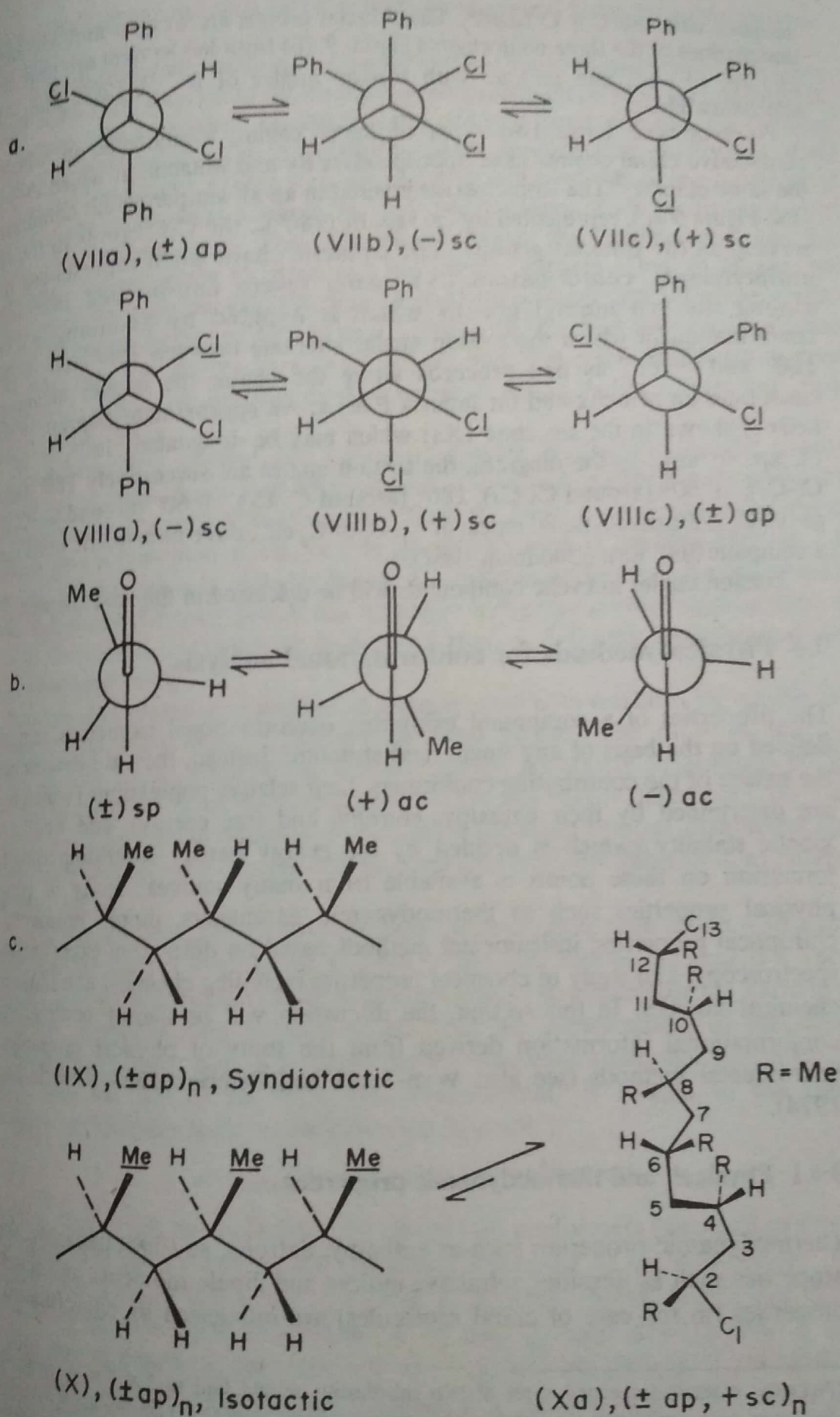


Figure 9.4 Klyne-Prelog nomenclature for torsion angles

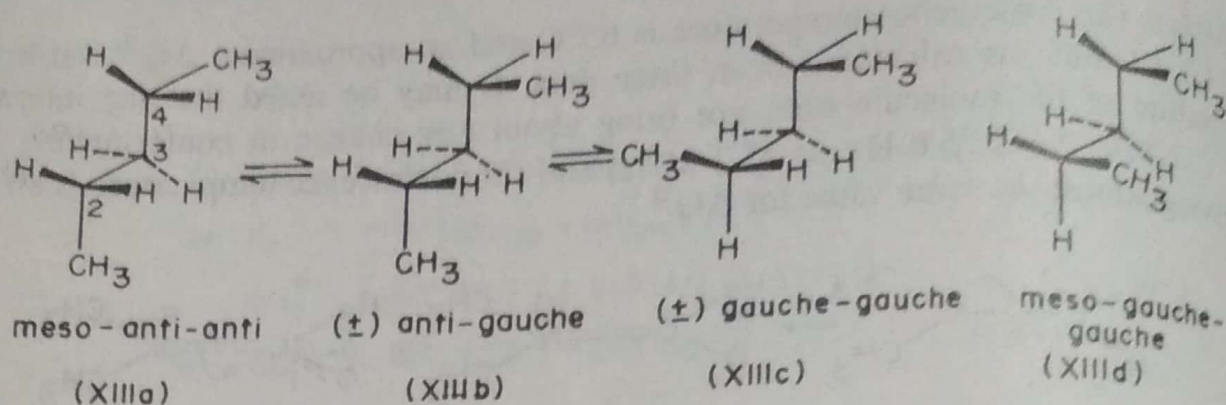
eclipsed with the C = O bond\*. The fiducial groups are oxygen and Me and the designations of the three conformers (Figure 9.4b) from left to right are respectively ( $\pm$ ) sp, (+) ac, and (-) ac with torsion angles of  $0^\circ$ ,  $+120^\circ$ , and  $-120^\circ$  approximately.

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<sup>†</sup>. The former exists layered in an all antiperiplanar conformation (IX, Figure 9.4c), represented by  $(\pm ap)_n$  or  $(180^\circ)_n$ , the C-C bonds in the chain serving as the fiducial groups. The isotactic chain when represented by all antiperiplanar conformation (X) incurs severe non-bonded interactions among the syn methyl groups which is avoided by assuming a helical conformation in which the torsion angles alternate between  $180^\circ$  and  $+60^\circ$  or  $180^\circ$  and  $-60^\circ$  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 (Xa) which may be designated  $(180^\circ, +60^\circ)_n$  or  $(\pm ap, +sc)_n$ . In the diagram, the torsion angles are successively  $180^\circ$  (around C<sub>2</sub>-C<sub>3</sub>),  $+60^\circ$  (around C<sub>3</sub>-C<sub>4</sub>),  $180^\circ$  (around C<sub>4</sub>-C<sub>5</sub>),  $+60^\circ$  (around C<sub>5</sub>-C<sub>6</sub>), and so on. C<sub>7</sub> is the translational repeat of C<sub>1</sub>, C<sub>8</sub> of C<sub>2</sub> etc., three monomeric units making a complete  $360^\circ$  turn (Goodman 1967).

Torsion angles in cyclic compounds will be discussed in the next chapter.

### 9.5.1 Conformations of alkanes

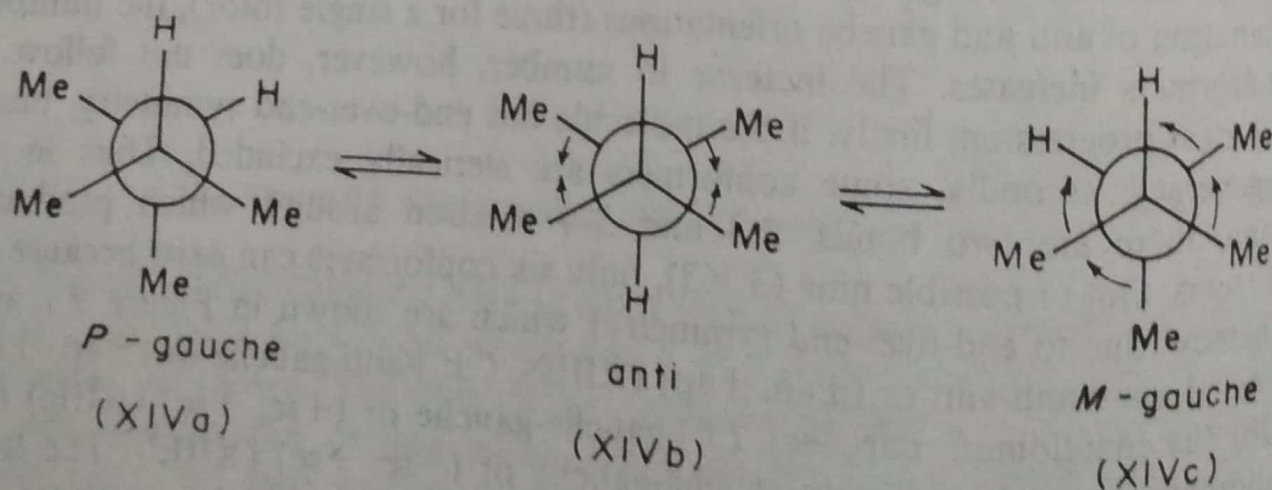
For straight chain hydrocarbons containing more than four carbon atoms, rotational isomerism takes place around more than one C-C bond (such molecules are called multiple rotors) and the nature and number of conformers may be considered in terms of constituent *n*-butane units. Generation of an anti conformation around an additional C-C bond does not increase the energy of the molecule but the formation of a gauche unit adds up approximately  $3.3 \text{ kJ mol}^{-1}$  of energy. While rotation around any single bond gives rise to three conformers as in *n*-butane, subject to symmetry consideration, no additional isomers are formed by rotation around bond connecting any terminal methyl group. As a result of various combination of anti and gauche orientations (three for a single rotor), the number of conformers increases. The increase in number, however, does not follow a geometrical progression; firstly, if the molecule has end-over-end symmetry, there is degeneracy; secondly, some conformers are sterically excluded. Thus in *n*-pentane, there are two bonds, 2-3 and 3-4 rotation around which produces conformers. Out of possible nine ( $3 \times 3$ ), only six conformers can exist because of degeneracy (due to end-over-end symmetry) which are shown in Figure 9.7 and designated *meso*-anti-anti or  $(\pm\text{ap}, \pm\text{ap})$  (XIIIa),  $(\pm)$ -anti-gauche or  $(\pm\text{ap}, +\text{sc})$  (XIIIb) (its enantiomer:  $\pm\text{ap}, -\text{sc}$ ),  $(\pm)$ -gauche-gauche or  $(+\text{sc}, +\text{sc})$  (XIIIc) (its enantiomer:  $-\text{sc}, -\text{sc}$ ), and *meso*-gauche-gauche or  $(-\text{sc}, +\text{sc})$  (XIII d). The last-named conformer, however, has synparallel methyls and is of high energy (ca  $16 \text{ kJ mol}^{-1}$ ) which leaves only *five* conformers appreciably populated. The anti-anti



**Figure 9.7** Conformations of *n*-pentane

conformer is given an arbitrary zero energy and the other two conformers (XIIIb) and (XIIIc) have 3.3 and 6.6 kJ mol<sup>-1</sup> of energy respectively. Newman projection formulae are inadequate to represent these conformers; instead, zigzag extended sawhorse formulae are used. Normal paraffins from C<sub>4</sub> to C<sub>12</sub> have been studied both in solid and liquid states by Raman and IR spectroscopy (Mizushima 1954). In the crystalline state, often a single conformer, the all-anti form is found but in the liquid or gaseous state, equilibrium among various anti-gauche combinations is established. As the chain length increases, e.g., in *n*-cetane, the statistical probability of having an all-anti conformation in the liquid or vapour state becomes very small and conformers with one or more gauche orientations predominate.

The conformations of branched chain alkanes are examined on a similar basis. In these cases, however, in addition to steric factor, bond angle deformations also play an important part. The cases of propane, 2-methylpropane, and 2,2-dimethylpropane have already been discussed. 2,3-Dimethylbutane provides an interesting case. It exists in an achiral anti (XIVb) and two enantiomeric gauche forms (XIVa) and (XIVc) (Figure 9.8) and all three conformers appear to be equally populated at all temperatures as evidenced from Raman, IR, and NMR spectra. The conformational free energy is, therefore, zero and the total concentration of the gauche form is twice that of the anti. Similar preference of gauche conformers is also observed in 1,1,2,2-tetrachloro- and 1,1,2,2-tetrabromoethanes (see later). This has been ascribed to a widening of the Me-C-Me and X-C-X angles (Thorpe-Ingold effect) which is easy in gauche but difficult in anti conformers (where it produces



Me-Me steric compression evident from the directions of arrows shown in Figure 9.8). There are two rotational barriers in these molecules. For 2,3-dimethylbutane, the values are 18.0 and 33.0 kJ mol<sup>-1</sup>, the higher one corresponding to two Me-Me eclipsings and one H-H eclipsing. Since rotation takes place through the path of least resistance, the gauche-gauche interconversion cannot take place directly (it necessitates crossing the higher energy barrier) but goes through the intermediacy of the anti form.

### 9.5.2 Conformations of halogenoalkanes

The conformations of a large number of halogenoalkanes have been studied by Raman, IR, and microwave spectroscopy and in some cases also by dipole moment measurements. Several points are of interest. The energy barriers in ethyl halides (CH<sub>3</sub>-CH<sub>2</sub>X, X = F, Cl, Br, and I) are remarkably similar in magnitude (around 14-15 kJ mol<sup>-1</sup>, Table 9.4) despite considerable difference in the size of the halogens. It appears that the effect of the increasing size is compensated by the correspondingly increasing bond lengths as the halogen changes from F, Cl, Br to I. The slightly higher values of the barrier heights compared to ethane (12.0 kJ mol<sup>-1</sup>) are consistent with the increased van der Waals radii of halogens compared to hydrogen. The extra energy is thus a result of a steric effect rather than of electronic origin.

*n*-Propyl chloride exists in an anti and two enantiomeric gauche conformers (Figure 9.9). In the liquid and gaseous states, the gauche conformers (XVb) and (XVc) predominate, the conformational free energy being 2.5 kJ mol<sup>-1</sup> in favour of the gauche as determined by microwave spectroscopy. Electron diffraction experiments show a torsion angle of 65-70° between Me and Cl in the gauche form. It is thought that, in this geometry, the two groups are at a distance where van der Waals attractive forces (London forces) rather than repulsive ones predominate so that the gauche conformer is preferred over the anti (XVa). Even when Me is replaced by Et as in *n*-butyl chloride, the gauche orientation (with respect to the C<sub>1</sub>-C<sub>2</sub> bond) is slightly favoured ( $\Delta G^\circ = 1.3$  kJ mol<sup>-1</sup>). These are interesting examples where the gauche forms are favoured due to van der Waals forces of attraction.

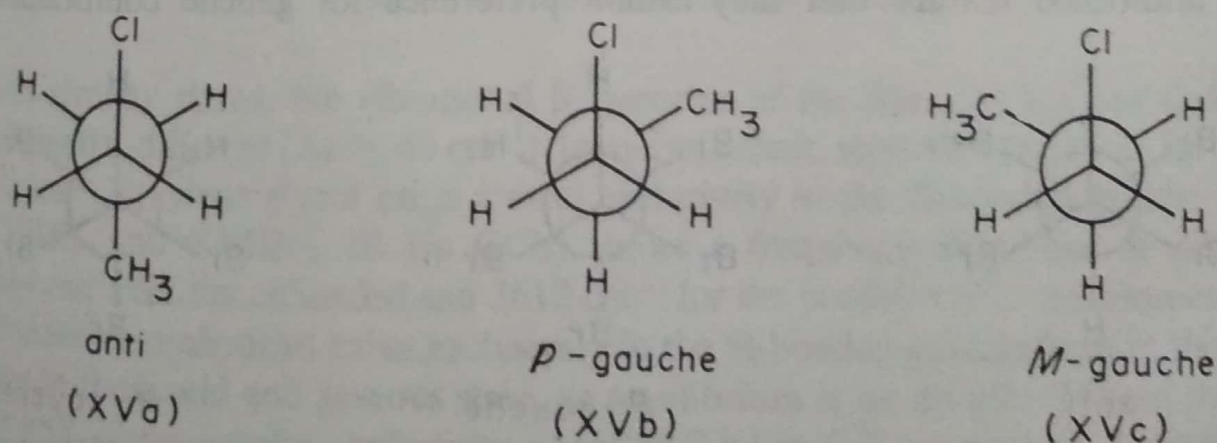


Figure 9.9 Conformations of *n*-propyl chloride

The conformations of 1,2-dihalogenoethanes (Figure 9.10) have been extensively studied by various physical methods especially by dipole moment measurement, Raman, IR, and microwave spectroscopy. In the gaseous state at 22°C, 1,2-dichloro- and 1,2-dibromoethanes contain 73 and 85% of the anti conformers respectively as against 67% for *n*-butane. The higher stability of the anti form (as XVIa) in comparison to *n*-butane is due to a combined effect of a steric factor (larger in the bromide than in the chloride) and an electronic interaction (dipole-dipole repulsion). In the liquid state or in polar solvents, on the other hand, the electrostatic repulsion decreases considerably due to the high dielectric constant of the medium and the ratio of gauche conformers (XVIb) and (XVIc) increases. In dichloroethane, the two conformers (anti and gauche) are almost equally populated in the liquid state whereas in dibromoethane, the gauche population is 35% corresponding to a conformational free energy of 3.5 kJ mol<sup>-1</sup> in favour of the anti. Similarly, for 1,2-chlorofluoro-, 1,2-bromofluoro-, and 1,2-fluoroiodoethane, the anti forms predominate in the gaseous state but the gauche forms become more in the liquid state. The barrier height in 1,2-dichloroethane (approximately 12.5 kJ mol<sup>-1</sup>) is very similar to that in ethane which means that H-H and H-Cl eclipsing interactions are similar in nature and that there is little H/Cl steric effect.

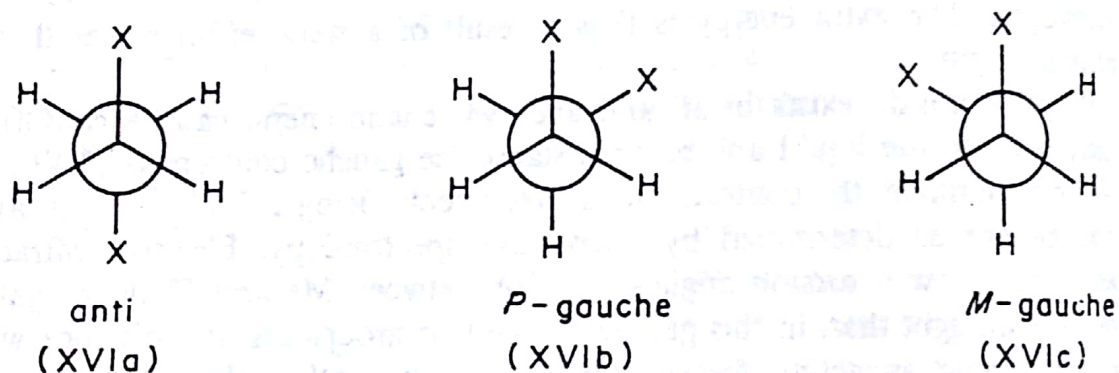


Figure 9.10 Conformations of 1,2-dihalogenoethanes

As the number of halogen substituents is increased, the barrier energy gradually increases from 15.5 kJ mol<sup>-1</sup> in ethyl chloride to 50-60 kJ mol<sup>-1</sup> in hexachloroethane, the 1,1,2,2-tetrachloro- and 1,1,2,2-tetrabromoethanes (Figure 9.11) have the additional feature that they exhibit preference for gauche conformations

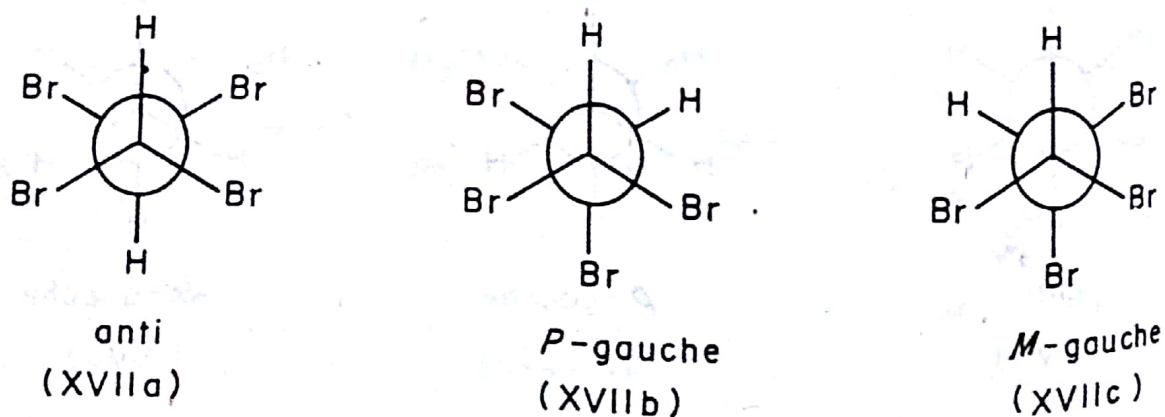


Figure 9.11 Conformations of polyhalogenoalkanes

(XVIIb) and (XVIIc) over the anti (XVIIa). Moreover, the tetrabromo-derivative gives two isomorphous crystals (depending on conditions) one containing the anti and the other containing the gauche conformer exclusively so that both forms can be studied by X-ray diffraction experiments.

### 9.5.3 Conformation and intramolecular hydrogen bonding

Intramolecular H-bonding between two vicinal groups confers an appreciable amount of stability ( $8-20 \text{ kJ mol}^{-1}$ ) to a conformer. For effective intramolecular H-bonding to occur, the donor and the acceptor groups (Chapter 1) must be close to each other which is possible only in the eclipsed or gauche conformation. In the eclipsed conformation, however, the atoms come within contact distance, so van der Waals repulsive forces come into play and make the conformation unstable. The gauche conformations with a torsion angle of  $60-70^\circ$  between the interacting groups are ideally suited for intramolecular H-bonding. The anti conformer with the two groups oppositely placed as in XVIIIa (Figure 9.12a) does not permit the formation of such a bond.

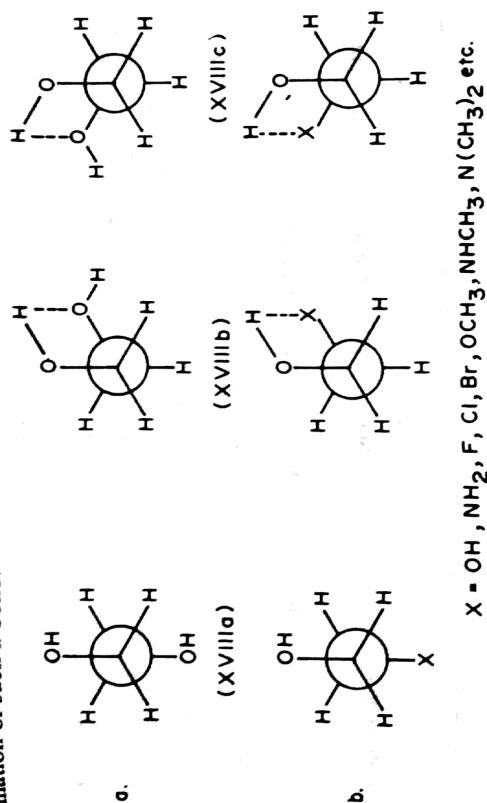


Figure 9.12 Conformations and H-bonding

As already stated, the vibrational frequencies of the free and bonded O-H are sufficiently different ( $\Delta\nu \approx 40 \text{ cm}^{-1}$ ) to permit their separate detection in dilute solution\*. Ethylene glycol exists almost exclusively in the H-bonded gauche forms (XVIIIb and XVIIIc). IR (in  $\text{CCl}_4$ ) shows a frequency difference of  $32 \text{ cm}^{-1}$  ( $3644 \text{ cm}^{-1}$  for the unbonded and  $3612 \text{ cm}^{-1}$  for the bonded OH). 2-Chloroethanol (ethylene chlorohydrin) exists exclusively in the H-bonded gauche form in the solid state; in the liquid and gaseous state, an equilibrium is set up with 15% of the anti and 85% of the gauche conformers ( $\Delta G^\circ = 4.0 \text{ kJ mol}^{-1}$ ). In general, 2-substituted ethanols of the type,  $\text{X-CH}_2\text{-CH}_2\text{-OH}$  where  $\text{X} = \text{OH}, \text{NH}_2, \text{F}, \text{Cl}, \text{Br}, \text{OCH}_3,$

\*To ensure the absence of intermolecular H-bonding.



NHCH<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub> etc. (Figure 9.12b) all have the preferred gauche conformation with OH and X forming intramolecular H-bonds. Usually the dihedral angle is slightly greater than 60°.

#### 9.5.4 Conformations of 1-substituted 3,3-dimethylbutanes

The conformations of a large number of monosubstituted 3,3-dimethylbutanes of the general formula (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>-CH<sub>2</sub>X (XIX) (Figure 9.13) around the 1-2 bond have been studied by <sup>1</sup>H-NMR (Whitesides et al 1967) and the conformational energies (ΔE) determined for different groups. The anti form (XXa) is in all cases more stable than the gauche (XXb) and the ΔE values (Table 9.5) thus give the relative magnitude of gauche interactions for different substituents. Since the gauche interaction in these cases essentially arises from steric factors, the values are also indicative of the effective size of the groups. Some of the interesting features are: (i) CH<sub>3</sub> and OH have similar interactions and so similar effective size (this is in variation with cyclic compounds). (ii) The conformational energy\* in the

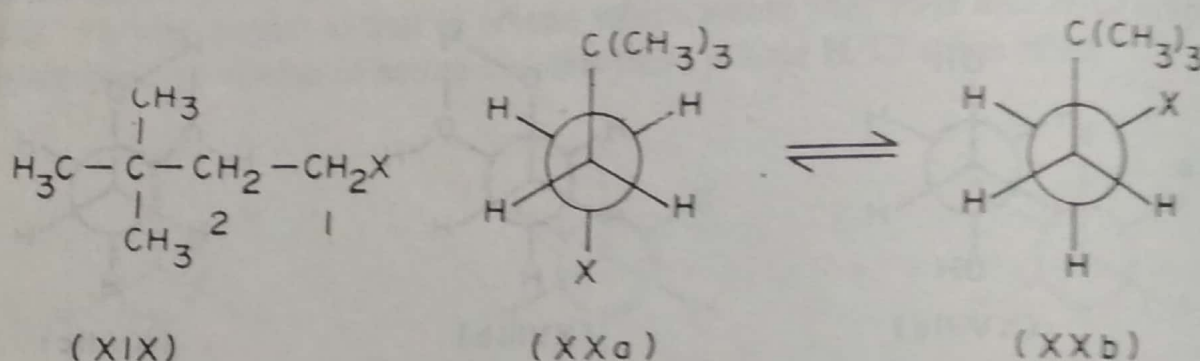


Figure 9.13 Conformations of (CH<sub>3</sub>)<sub>3</sub>C-CH<sub>2</sub>-CH<sub>2</sub>X

Table 9.5 Conformational energies of some 1-substituted 3,3-dimethylbutanes<sup>a</sup>  
(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>-CH<sub>2</sub>X

X =	ΔE, kJ mol <sup>-1</sup>	X =	ΔE, kJ mol <sup>-1</sup>
H	0.00	NH <sub>2</sub>	4.53
CH <sub>3</sub>	2.94	CO <sub>2</sub> H	4.48
C <sub>6</sub> H <sub>5</sub>	6.93	CO <sub>2</sub> Me	3.70
F	2.60	O-C <sub>6</sub> H <sub>5</sub>	2.50
Cl	4.51	O-SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br(p)	2.50
Br	5.49	SMe	6.16
I	6.76	S-C <sub>6</sub> H <sub>5</sub>	6.21
OH	3.07	SCN	6.29
CN	3.49	CONH <sub>2</sub>	5.37

<sup>a</sup> Taken from G.M. Whitesides, J.P. Sevenair, and R.W. Goetz, *J. Amer. Chem. Soc.*, 1967, **89**, 1135.

\*These conformational energies should not be confused with conformational free energies of substituents in cyclohexane discussed in the next chapter.

halogen series increases as the size of the halogen increases from fluorine, chlorine, bromine to iodine which is expected. (iii) The effective size is determined mainly by the first atom through which the substituent is linked as evidenced from the fact that  $\text{SCH}_3$ ,  $\text{SCN}$ , and  $\text{SC}_6\text{H}_5$  have similar conformational energy and so also have  $\text{O-C}_6\text{H}_5$  and  $\text{O-SO}_2\text{C}_6\text{H}_4\text{Br}$  (*p*).

**Conformation around  $\text{sp}^3\text{-sp}^2$  and  $\text{sp}^2\text{-sp}^2$  bonds**