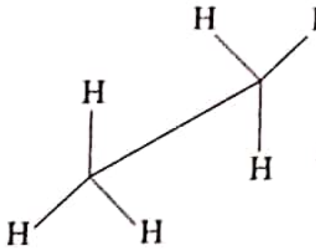
1.5.1 Rotation around a single bond

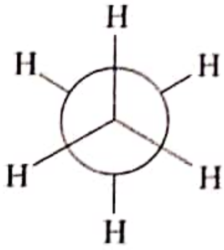
According to the *principle of free rotation* of classical stereochemistry, rotation around a single bond was considered to be free. Strictly speaking, this would mean that the potential energy of the molecule is independent of the dihedral angle. However, calculation of enthalpy and entropy of ethane based on statistical mechanics showed that in order to bring agreement between the calculated and experimental values, an energy barrier of 12.5 kJ mol^{-1} has to be assumed. The diagram (Figure 1.5) shows the



(s)

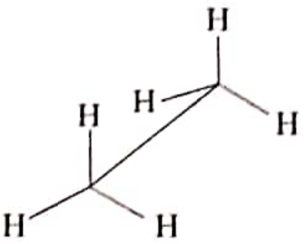
(XVIII)

≡



(s)

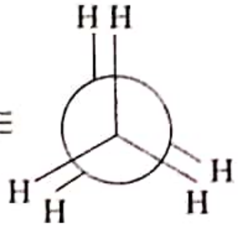
(XIX)



(e)

(XX)

≡



(e)

(XXI)

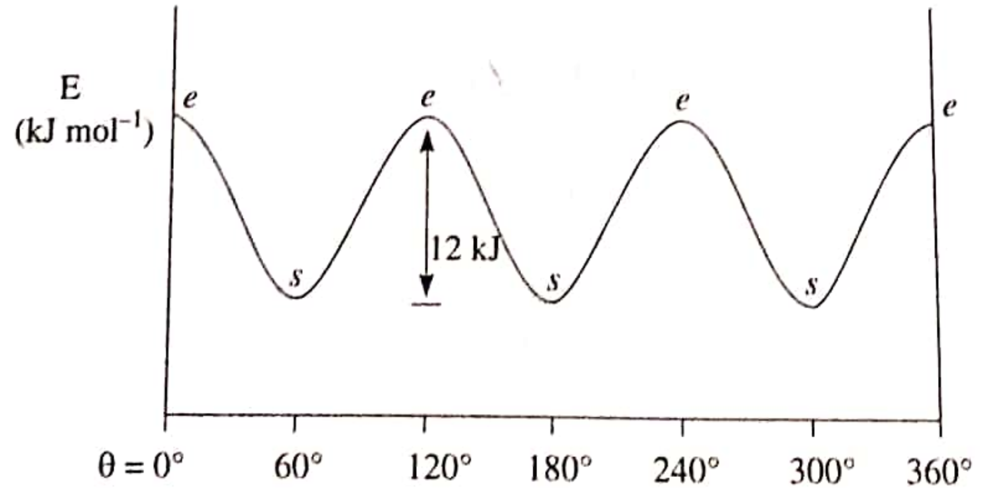


Figure 1.5 Restricted rotation in ethane

change of enthalpy or the energy barrier with the change of dihedral angle from 0° to 360°. 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 formula 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 along the line of vision and cannot be seen. The other bonds are oriented radially making 120° angle with one another. The 109.5° angle of a tetrahedral carbon and 120° angle of a trigonal carbon would appear as 120° and 180° 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°and 0° 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 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 nm) is almost equal to twice the value of van der Waals atomic radius of hydrogen (0.12 nm) (see Chapter 9).

1.5.2 Rotation around a double bond

Rotation around a double bond is highly restricted because it disrupts a π 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° and 180° respectively (see Newman projection formulae, *a* and *b* viewed along C=C bond). They differ in the relative disposition of the methyl groups and are called *cis* and *trans* isomers respectively. This type of stereoisomerism will be discussed in more general terms later. Starting from the structure (XXII*a*), an increase of dihedral angle to 90° breaks the π bond completely resulting in a high-energy species (XXIV*c*) in which the two *p* orbitals are mutually perpendicular. A further rotation of 90° regenerates the π bond giving the trans isomer (XXIII*b*) (which is more stable than the *cis* isomer by approximately 4.2 kJ mol^{-1} due to the absence of non-bonded interaction between the two methyl groups) with a large drop of energy (see the diagram). Another energy maximum occurs at dihedral angle 270° corresponding to a species (*c*′) which is the mirror image of (XXIV*c*) and finally, the molecule returns to the original structure (XXII) after a rotation of 360°. The energy barrier separating the two isomers is very high and as a result, interconversion between them is not possible under ordinary conditions. Other double bonds, *e.g.*, C=N, N=N behave similarly and may lead to *cis-trans* isomerism.

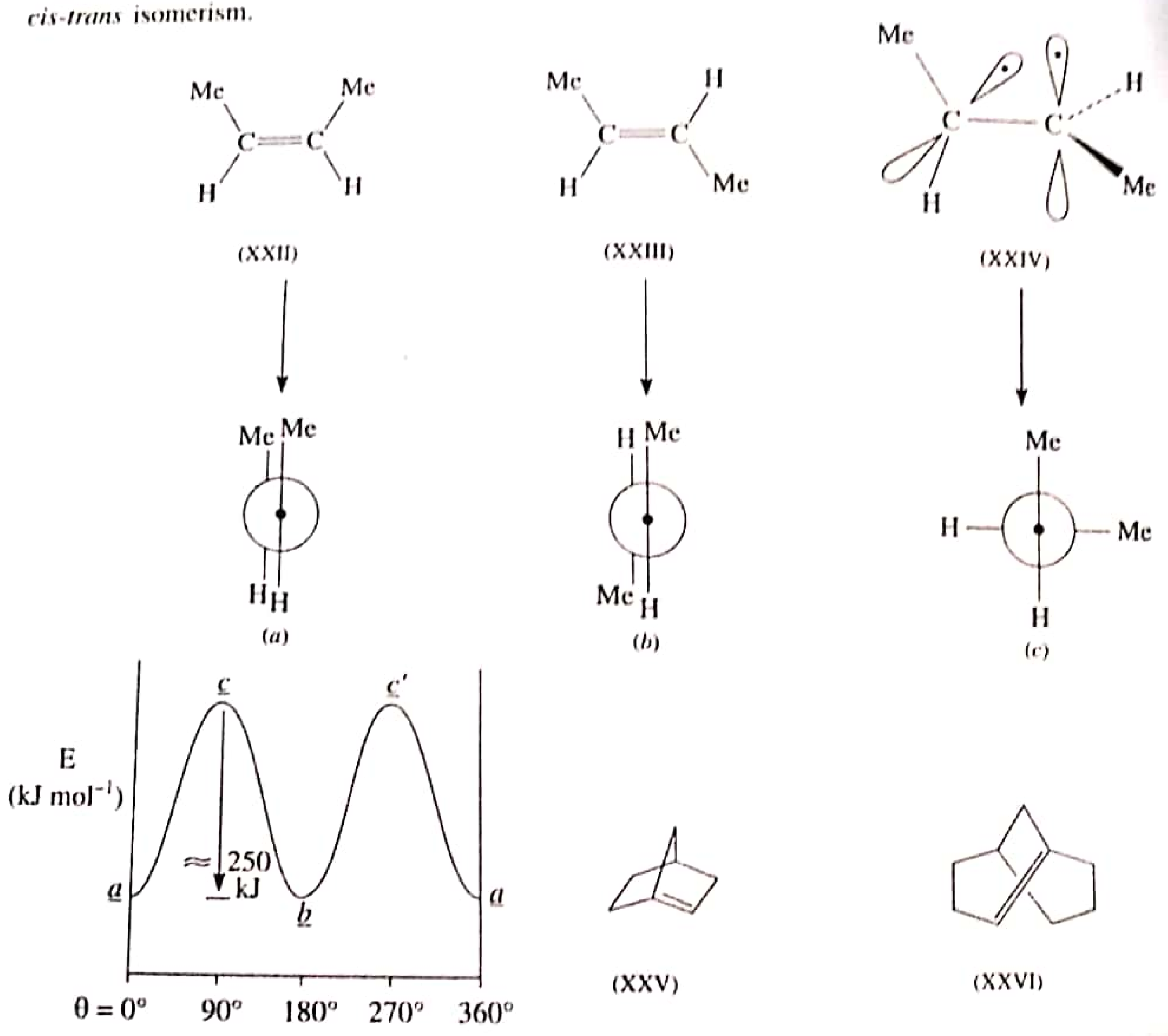


Figure 1.6 Restricted rotation around double bond. Examples of Bredt's rule

Bredt's classical rule which states that double bond cannot exist at a bridgehead position finds its justification in the special geometrical requirement of a double bond. Thus the bicycloheptene (XXV) is not formed because the planarity required by the π bond cannot be maintained in the rigid ring system. On the other hand, the bicyclononene (XXVI) with a bridgehead double bond is stable. Here the planarity of the π bond is accommodated by the puckering of the large ring. Many exceptions to Bredt's rule are now known.*