

2 Ethane

Aims

In this chapter you will learn about the rotation about the carbon-carbon single bond of ethane and the effect of rotation on the shape and energy of the ethane molecule. The study of the relation between the rotation of single bonds and the molecular structure and that with the molecular energy is called **conformational analysis**.

With the aid of the Newman projection formula, the conformational analyses of propane, butane and polysubstituted ethanes will be presented. Naming the conformers will also be presented by expanding the sequence rule.

New terms and concepts

flying-wedge representation
 perspective representation
 Newman projection
 conformational analysis
 dihedral angle-energy diagram
 conformer
 twist angle
 twist angle-energy diagram
eclipsed
skew
anti
gauche
periplanar
clinal

Goals of this chapter

After you master this chapter successfully, you will be able to do the following:

- 1 To draw the Newman projection of ethane in any conformation.
- 2 To draw a dihedral angle-energy diagram in describing the energy change of ethane by the rotation about a single bond.
- 3 To distinguish *eclipsed* and *staggered* conformations.
- 4 To distinguish two *staggered* conformers, *anti* form and *gauche* form, in the conformational analysis of butane.
- 5 To understand the nomenclature of conformers based on the sequence rule.

2.1 The Newman Projection

The rotation about the C-C single bond of ethane and related molecules to induce a change of molecular shape is well understood. It is necessary, however, to establish a set of rules beforehand in order to express the change of three-dimensional structures with two-dimensional drawings.

Schematic Drawings

The first step in expressing molecular structures in a two-dimensional way is the use of schematic drawings; *i.e.*, drawing molecular structures as they appear to be. In order to stress the three-dimensional nature, several conventions have been devised. Perspective and flying wedge drawings are typical examples.

2.2 Conformational analysis of ethane

Then how can we describe the relation between **1** and **2**? They are stereoisomers of each other since the spatial relation among the eight atoms constituting each ethane differ. The difference is, however, not the same as the one observed for **14** and **15** of Ch. 1 (the two enantiomers of CHFCIBr). Compounds **14** and **15** are not interconvertible without breakage and reunion of some chemical bonds. On the other hand, **1** and **2** in this chapter are interconvertible by the rotation about a single bond without breaking a bond. Such cases as **1** and **2** are referred to as having different **conformations**.

How can we distinguish conformations **1** and **2**? Rotation about the C-C bond will cause a change in the dihedral angle ϕ and consequently the distance between H_A and H_B . If the distance between the two hydrogen atoms becomes short, the potential energy of the molecule will increase because the steric repulsion will have increased. When the dihedral angle $\phi = 0^\circ, 120^\circ$ and 240° , it becomes maximal; when the dihedral angle $\phi = 60^\circ, 180^\circ$ and 300° , it becomes minimal. Thus, the plot of ϕ and the potential energy will yield the dihedral angle-potential energy curve given in Fig. 2.3

A study such as that of the change of molecular structure and energy caused by a rotation of the C-C (and other) single bond is called **conformational analysis**.

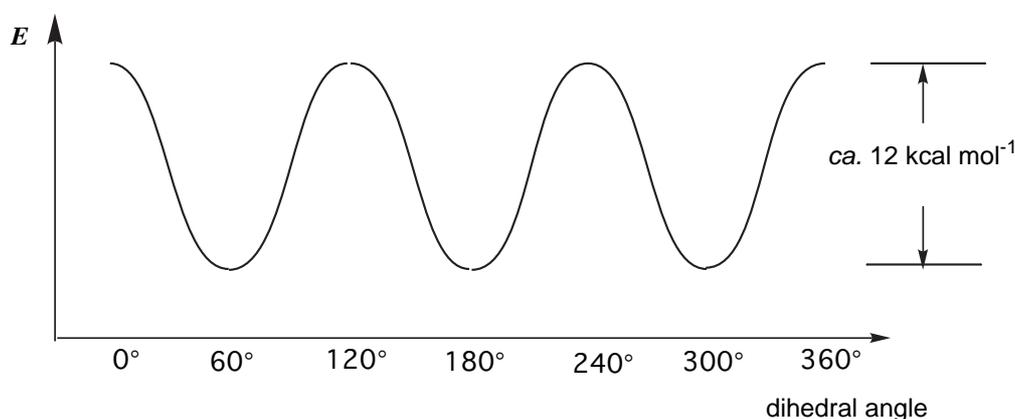


Figure 2.3 Dihedral angle – energy diagram of ethane

S2.1 Conformational analysis

conformational analysis: a study of the change of molecular structure (accompanied by the change of energy and properties) caused by a rotation about a single bond.

the dihedral angle-potential energy diagram: a plot of potential energy (abscissa) vs. dihedral angle (horizontal); indispensable for conformational analysis of simple molecules.

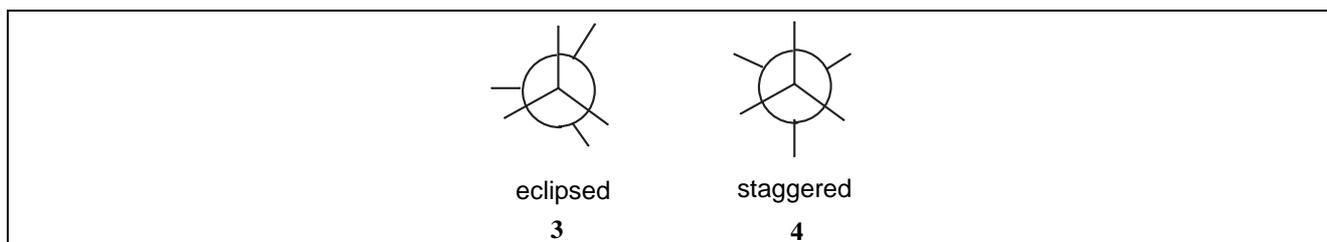
Potential energy of ethane is maximal when $\phi = 0^\circ, 120^\circ$ and 240° , and minimal when $\phi = 60^\circ, 180^\circ$ and 300° . The structure for the former is called **staggered (4)** and that for the latter **eclipsed (3)**.

The potential energy difference between the two forms is *ca.* 12 kJ mol⁻¹ (2.86 kcal mol⁻¹). Conformations corresponding to the structures having minimal energy are called **conformational isomers** or simply **conformers**. In this book we use the word conformer throughout.

S2.2 Eclipsed and staggered forms.

eclipsed form **3**: conformation of ethane and analogs with $\phi = 0^\circ, 120^\circ$ and 240°

staggered form **4**: conformation of ethane and analogs with $\phi = 60^\circ, 180^\circ$ and 300°

**Q2.1**

How many conformations does the ethane molecule have?

Q2.2

How many conformers does the ethane molecule have?

A2.1

Indefinite. By changing the dihedral angles minutely, you can obtain as many conformers as you like.

Q2.3

Do a conformational analysis of propane $\text{CH}_3\text{-CH}_2\text{-CH}_3$ and draw the dihedral angle-potential energy diagram. The dihedral angle is defined as the angle made by the C-CH_3 bond and the C-H bond.

A2.2

2. The conformers with $\phi = 60^\circ$, 180° and 300° are also identical.

A2.3

The dihedral angle-energy diagram will be much the same as Fig. 2.3. Since the $\text{CH}_3\text{---H}$ interaction is necessarily larger than the H---H interaction, the energy difference between the *staggered* and *eclipsed* conformations is larger than that for ethane. Both curves have a similar cycle of 120° . It must be mentioned that another C-C bond should also rotate and will cause a more complicated structural change. This process is not considered here.

2.3 Conformational analysis of butane

Although propane has much the same dihedral angle-energy diagram as that of ethane, a considerably different result will be obtained when conformational analysis of butane is done in relation to the rotation of the central C-C bond. When the potential energy of the molecule is plotted against the dihedral angle made by the two C-CH_3 bonds, there are obtained two forms with maximum energies (A and C of Fig. 2.4) and two conformers with minimum energies are obtained (B and D of Fig. 2.4).

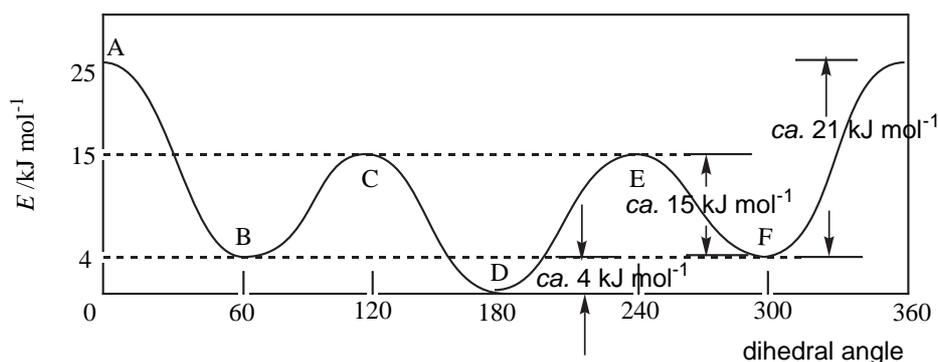
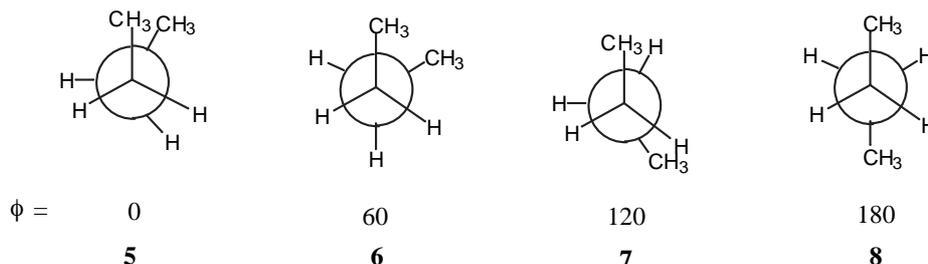


Fig. 2.4 The dihedral angle-potential energy diagram of butane.

The Newman projection corresponding to forms A-D is shown below (**5-8**). In the case of ethane, the *staggered* and *eclipsed* conformations can sufficiently describe the features of its conformational analysis. In the case of butane, however, two conformations are not enough to describe the features of the diagram. The dihedral angle of one of the *eclipsed* forms, **5**, is $\phi = 0^\circ$. This form is called *cis*. The dihedral angle of the other *staggered* form, **6**, is $\phi = 60^\circ$. This form is called *gauche*. The other one, **8**, with $\phi = 180^\circ$ is called *trans* or *anti*.

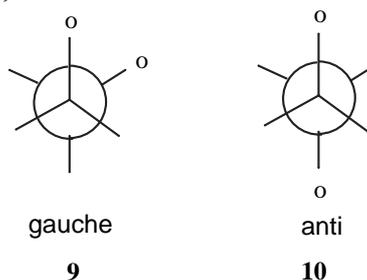
Because of the proximity of two methyl groups, **5** and **6** have larger energies than **7** and **8**, respectively. Cases will be discussed later where this treatment is not applicable because of more complicated structures.



S2.3 *Gauche* and *anti* forms.

gauche form: conformation of 1,2-disubstituted ethanes with $\phi = 60^\circ$ (or 300°).

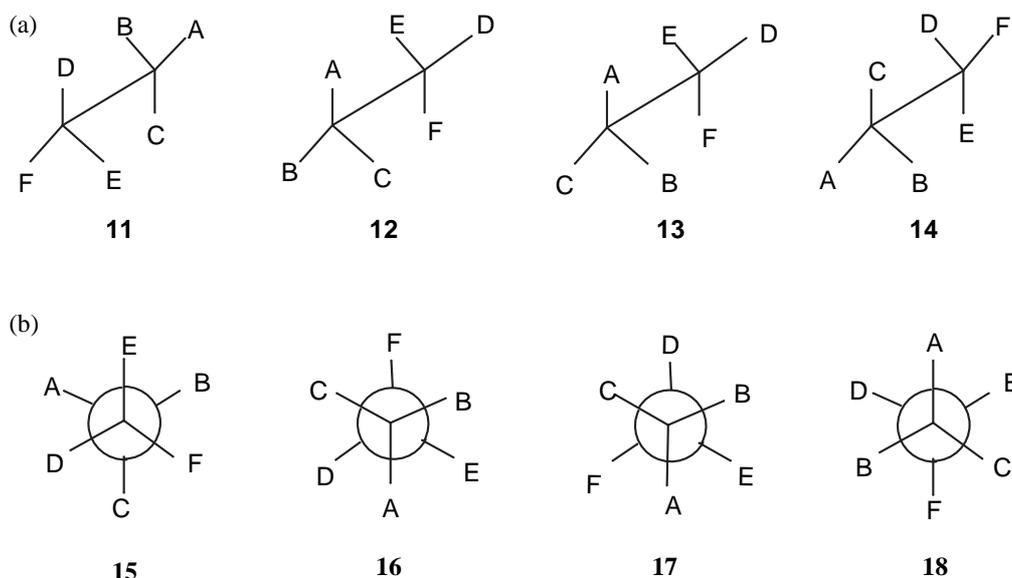
anti(trans) form: conformation of 1,2-disubstituted ethanes with $\phi = 180^\circ$.



One can draw many Newman projections for a given molecule. For an ethane derivative ABC-CDEF, projection can be done either from the ABC side (**16**) or from the DEF side (**15**). In addition, there are many rotational isomers (rotamers) in relation to the rotation about the C-C bond. Much the same is true for perspective drawings (**11**)-(14).

Q2.4

How many conformers are drawn (in different ways) with the perspective method (**11-14**) or Newman projection?



□

A2.4

(a) 2 (11 = 13, 12 = 14), (b) 3 (15 = 16) □

Nevertheless, we should not jump to the conclusion that we can separate the two conformers of butane in the ratio that we calculated. In order to isolate two interconvertible compounds such as **6** and **8** at room temperature, the energy barrier of interconversion (the energy difference between **6** and **8** or **5** and **7** in the case of butane) should be at least 100 kJ mol^{-1} .

As you can guess from Fig. 2.4, the actual energy difference is at most $15\text{-}20 \text{ kJ mol}^{-1}$. The interconversion takes place freely at room temperature.

2.4 Relative abundance of conformers

Ethane has two conformers; *eclipsed* and *staggered*. Does then ethane consist of two equal amounts of these two conformers? Definitely no. There are many other species with a different conformation. Furthermore, the two conformers have different steric energy, and hence the relative population of the two conformers may be different.

This situation can be visualized if we assume that the dihedral angle-energy diagram is a kind of **reaction profile**, which is a plot of the energy change of the system associated with the progress of the reaction. The vertical coordinate of a reaction profile, the reaction coordinate, corresponds to the dihedral angle of a dihedral angle-energy diagram. The *eclipsed* form is equivalent to the activated complex of a chemical reaction. Such a high-energy species will have a very short lifetime, and in almost all cases, it is impossible to isolate that species. In addition to the case of ethane, the *eclipsed* form for propane and butane is an intermediate of a reaction that has a very short lifetime.

One can assume that ethane exists most of the time as the most stable *staggered* form. In the case of butane there are two *staggered* forms, and hence it exists as a mixture of these two *staggered* forms. In such a case the relative amounts of the two *staggered* forms will depend on the difference in the Gibbs free energies ΔG . Generally speaking, for an equilibrium $A \rightleftharpoons B$, ΔG is expressed by the following equation

$$\Delta G = -2.303 RT \log K \quad (2.1)$$

where K is the equilibrium constant ($K = [B]/[A]$), R the gas constant ($= 1.98 \text{ cal deg}^{-1} \text{ mol}^{-1}$) and T the absolute temperature.

S2.4 ΔG and the relative amounts. The relation between the value of ΔG and the population of

conformers A and B are tabulated below.

K (298K)	2	3	4	5	10	20	100	1000	10000
amount of the more stable isomer(%)	67	75	80	83	91	95	99	99.9	99.99
ΔG (kJ mol ⁻¹)	1.71	2.72	3.43	3.97	5.85	7.52	11.3	17.1	23.0

Q2.5

Suppose we can consider that the difference of potential energy between the *gauche* form and *anti* form of butane is approximately equal to the difference of free energy. Calculate the population of the two conformers at the room temperature (25°C). □

Q2.6

If the difference in potential energy between the *gauche* form and the *anti* form of butane is higher than 100 kJ mol⁻¹, we should be able to isolate the more stable butane conformer at room temperature. How many varieties of conformers may be isolated? Guess the relation of their structures. □

A2.5

From Fig. 2.4, the difference of free energy is 4 kJ mol⁻¹, which is equal to $(4 \times 10^3/4.18)$ cal mol⁻¹. We can then obtain the following equation by substituting appropriate values into the equation given above.

$$(4 \times 10^3/4.18) (\text{cal mol}^{-1}) = -2.303 \times 1.98 (\text{cal deg}^{-1} \text{mol}^{-1}) \times 298 (\text{deg}) \log K$$

$$\therefore \log K = 0.692; K = 4.95$$

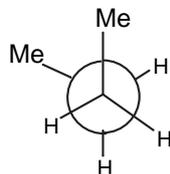
If we take the molar ratio of the *gauche* form as x , then $(1 - x)/x = 4.95$; $x = 0.168$

Finally, we can conclude that the *anti* form is *ca.* 17% and the *gauche* form *ca.* 83%, which is in qualitative agreement with our prediction. □

This does not, however, mean that one can separate butane into the *anti* and *gauche* forms. In order to separate at room temperature two rapidly exchanging species, *e.g.*, **6** and **8**, the barrier for the exchange, in the case of butane, the energy difference between **6** and **8** or **5** and **7**, should be at least as large as 100 kJ mol⁻¹. As is indicated in Fig. 2.4, the energy difference is *ca.* 15-20 kJ mol⁻¹, indicating that at room temperature the exchange is very rapid and separation is impossible.

A2.6

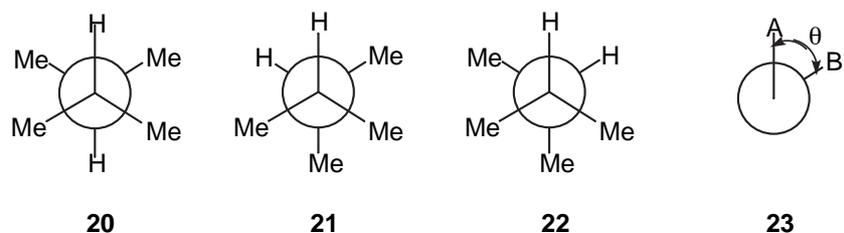
3; **6**, **8** and **19** ($\phi = 270^\circ$). All are conformers of one another. You should confirm, with the aid of the molecular model, that **6** and **19** are not identical but enantiomers each other.



□

2.5 Stereochemical nomenclature of ethane derivatives

We have already learned several terms, such as *gauche*, *anti*, *staggered* or *eclipsed*, to name the conformers based on the Newman projection. These are, however, insufficient when a more complex molecule is involved. For instance, there are three *staggered* forms for 2,3-dimethylbutane as shown below. It is impossible to define these as *gauche* or *anti* as long as we use the relations of methyl groups as the standard.



A systematic nomenclature has been proposed which could be applicable to such complex cases. For a four-atom system A-C₁-C₂-B, a **torsion angle** θ (**23**) is defined. Atoms C₁ and C₂ may be other types of atoms, but for simplicity we take these two as carbon atoms.

The definition of torsion angle is as follows.

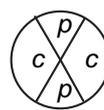
- 1) We look at the molecule along the C₁-C₂ axis as shown in **23**
- 2) Rotate the A-C₁ bond so that A overlaps B.
- 3) The torsion angle is defined as the angle of rotation necessary to overlap A with B.
- 4) The torsion angle is positive if the required rotation is clockwise, and negative if the rotation is counterclockwise.

It is important to notice that the torsion angle has a sign though the dihedral angle does not. Hereafter we shall use the torsion angle as far as possible in this textbook.

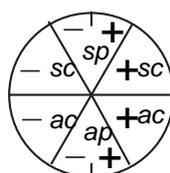
Ligands A and B are chosen from the ligands bonded to C₁ and C₂, respectively

- 1) If all three ligands are different, the priority is determined by the sequence rule.
- 2) If two ligands are identical, the rest are chosen for A and B regardless of the priority based on the sequence rule.
- 3) If three ligands are identical, the one associated with the smallest torsion angle is chosen.

In practice, the torsion angle of ethane derivatives is not necessarily a multiple of 60°. Hence, the value of the torsion angle itself is not included in the stereochemical names. A circle (torsion angle = 360°) is divided into several sections as is shown in **24-26**, and each section is given a name. By combining these names, a system of nomenclature of ethane derivatives is established.

**24****25****26**

The upper half of the circle is *syn* region, and the lower half is *anti* region (*cf.* **25**). The *p* of **26** stands for the *periplanar* region, and *c* for the *clinal* region. By combining these regions, you can obtain **27**.

**27**

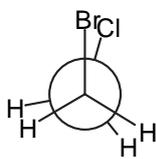
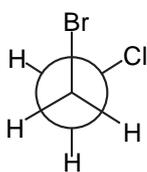
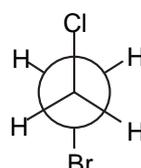
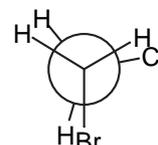
The essentials of this nomenclature will be summarized in S2.5.

S2.5 The stereochemical nomenclature based on the rotation about a single bond.

torsion angle θ	name
$0 \pm 30^\circ$	\pm synperiplanar (\pm sp)
$\pm 30^\circ \sim +90^\circ$	+synclinal (+sc)
$+90^\circ \sim +150^\circ$	+anticlinal(+ac)
$+150^\circ \sim +180^\circ$	+antiperiplanar (+ap)
$-30^\circ \sim -90^\circ$	-synclinal (-sc)
$-90^\circ \sim -150^\circ$	-anticlinal (-ac)
$-150^\circ \sim -180^\circ$	-antiperiplanar (-ap)

Q2.7

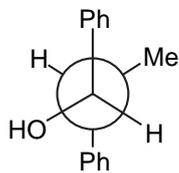
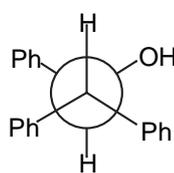
Compounds **28** ~ **31** have two halogen atoms as substituents. Define the conformation of each compound in terms of (a) *staggered* – *eclipsed* and (b) *sp*, *ap*, *etc.*

**28****29****30****31**

□

Q2.8

Define the conformation of the two compounds shown below.

**32****33**

□

A2.7

28 eclipsed, \pm sp, **29** staggered, +sc, **30** staggered, \pm ap (you may answer simply ap) **31** eclipsed -ac. □

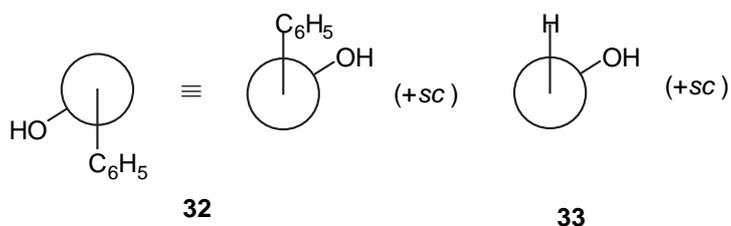
Q2.9

Define the conformation of all conformers of butane 5~8, and two isomers with $\theta = -60^\circ$ and -120° , in terms of *sp*, *ac*, *etc.* □

A2.8

32 +sc (Ph and OH are the reference ligands.)

33 +sc (H (not Ph) and OH are the reference ligands.) \equiv



□

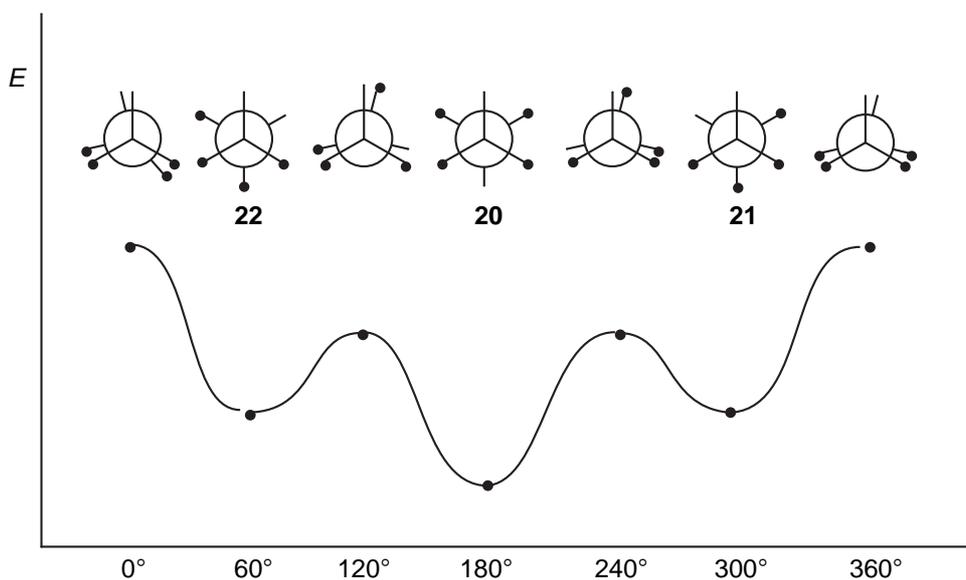
Q2.10

Sketch the torsion angle-energy diagram (like Figs. 2.3 and 2.4) of 2,3-dimethylbutane. Show the Newman projection of the relevant conformer when the energy is maximal or minimal. □

A2.9

Compound	5	6	7	8	(-60°)	(-120°)
θ	0°	60°	120°	180°	240°	300°
name	$\pm sp$	+sc	+ac	$\pm ap$	-ac	-sc

□

A2.10

The energy barrier for the interconversion $21 \rightarrow 20 \rightarrow 22$ is *ca.* 18 kcal mol⁻¹, and that for the interconversion $21 \rightarrow \pm sp \rightarrow 22$ is *ca.* 33 kcal mol⁻¹. □