Conformations of acyclic compounds Part-II

Paper-C5 T

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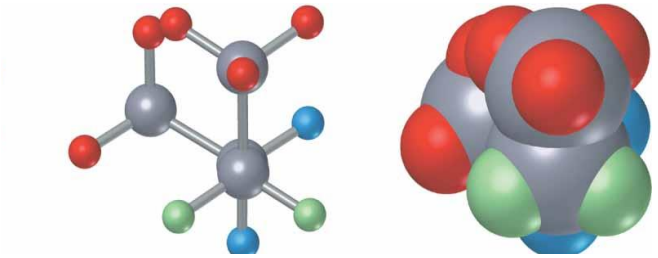
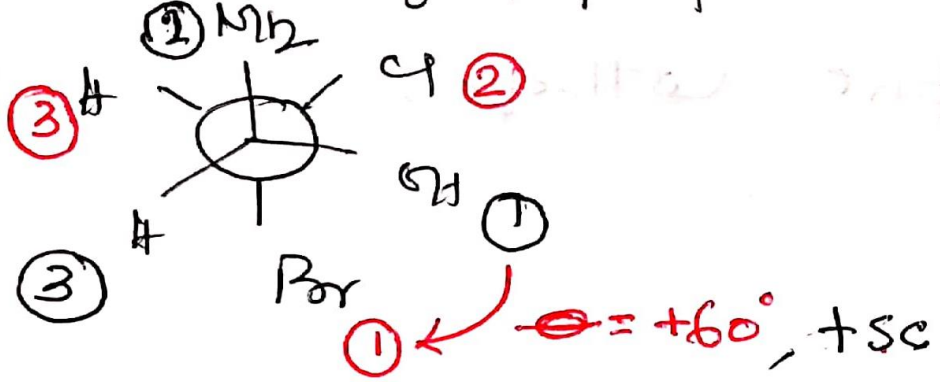


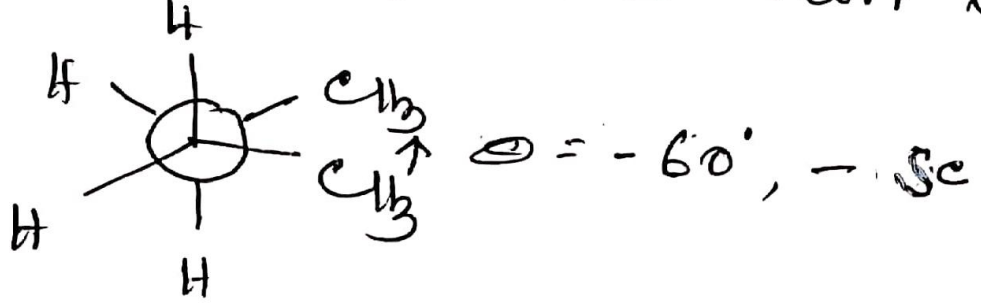
Klyne Prelog Terminology

Reference groups.

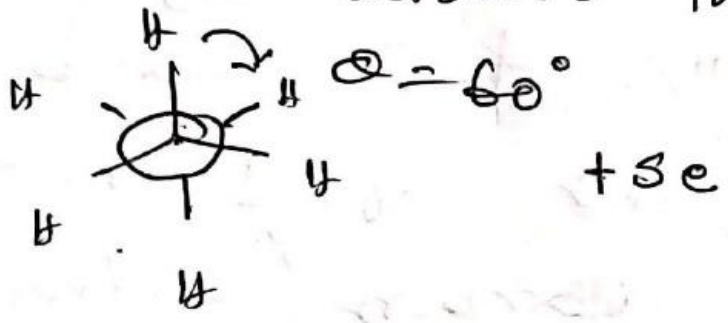
A. If all substituents in a set are different, selection is done on the basis of CIP rule. i.e from 1st gr of front to 1st gr of back



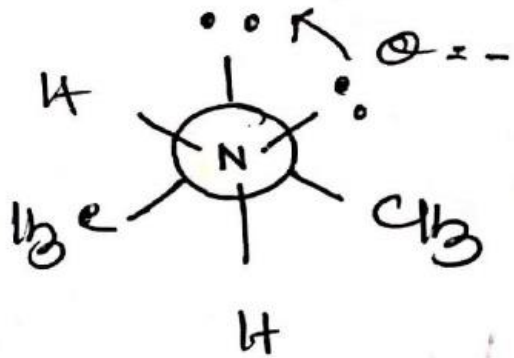
B. If two substituents in each set are identical then choose the non identical gr



C If all substituents are identical in a set then choose the atoms that make smallest torsion angle.

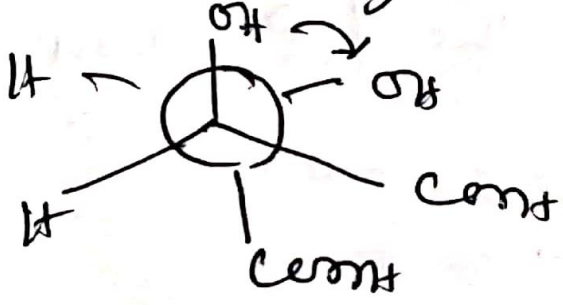


D If A and B in X-A-B-Y are trigonal centres bearing a lone pairs of electrons, then the L.P can decide the description

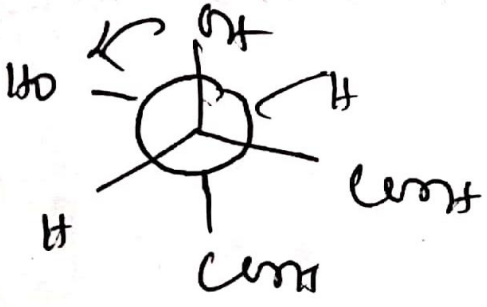


P-M Descriptor

First select the gr of highest priority on each carbon. Then look from the front carbon to the back. The rotation from gr 1 on front carbon to gr 1 of back carbon (minimum angle) is clockwise, the description will be P (Plus) and anticlockwise will be M (minus)



P

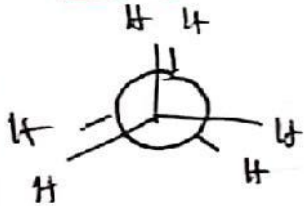


M.

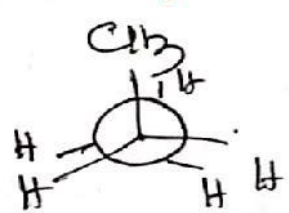
[For other compounds follow the selection rule for reference gr of Klyne-Prelog system.]

Propane, 2-methyl propane, 2,2-dimethyl propane have the same type of torsional curve as that of Ethane. But the energy diff. between Eclipsed and Staggered increases from ethane to 2,2-dimethyl propane.

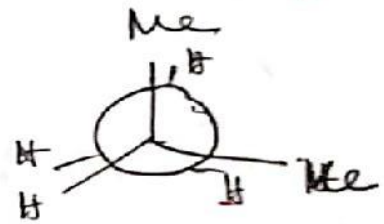
Ethane



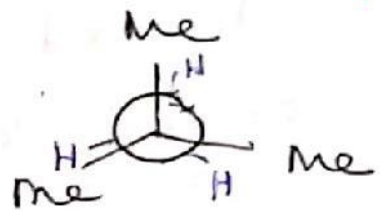
Propane.

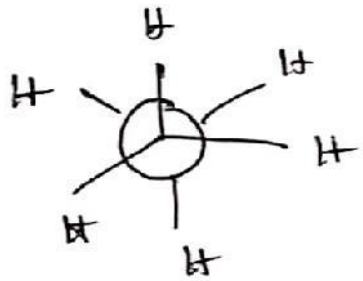


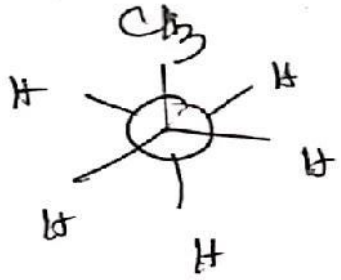
2-methyl propane

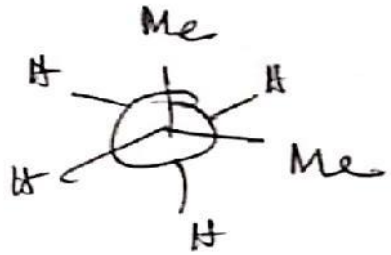


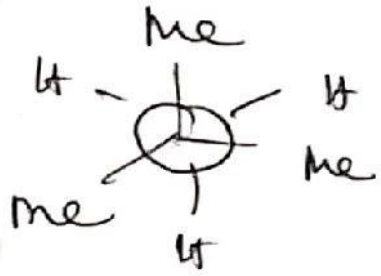
2-2-dimethyl propane











$\Delta E = 12.4$ kJ/mole

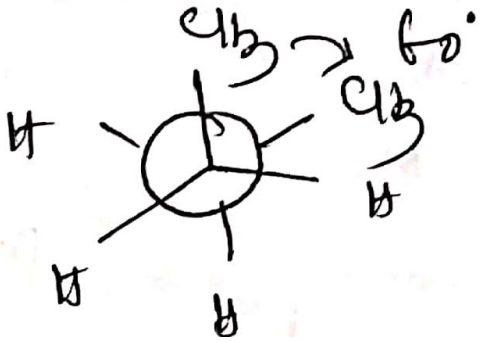
14.2 kJ/mole

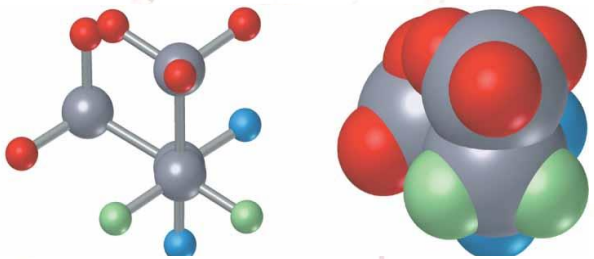
16.2 kJ/mole

19.5 kJ/mole (4)

Butane-Gauche Interaction

Comparison of energy of conformations, "anti" and "gauche", shows that "gauche" becomes destabilised by an amount of ~ 3·3 Kj/mole. This amount of energy represents the steric interaction energy of two Me groups at a torsion angle of ~ 60° by comparison with anti position, known as Butane gauche interactions.





Calculation of % of *anti* and *gauche* forms of n-Butane at 298°K :

The populations of the various conformers are related to their energy differences by the equation .

$$\Delta G^\circ = -RT \ln K \quad \text{---------- Eqn. 5. 7}$$

Where ΔG°, the conformational free energy, is equal to the excess of standard free energy of one conformer over that of the minimum energy conformer.

For the case of *n*-butane, the equilibrium *anti* $\rightleftharpoons$ *gauche* has $\Delta H^\circ = -0{\cdot}8$ kcal/mole, (3·36 $kJmol^{-1}$). In this case there is a statistical factor of 2 which favours the *gauche* form, (since there are two enantiomeric *gauche* conformers) leading to an entropy advantage of $R\ln 2$ for the latter.

Thus , $\Delta S^\circ = -R\ln 2$ ---------- Eqn. 5. 8

Now from the relation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ---------- Eqn. 5. 9

at 298°K, $\Delta G^\circ = -0{\cdot}8$ kcal/mol $- (-RT1n2)$

$= -0.8$ kcal/mol + 0.41 kcal/mol

$= -0{\cdot}39$ kcal/mol. ($\equiv 1.64$ $kJmol^{-1}$)

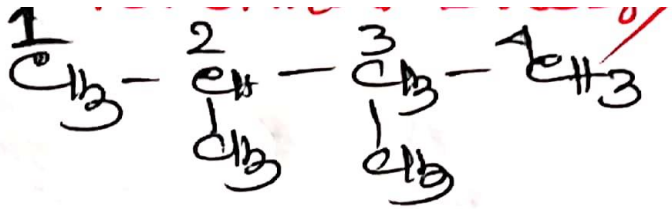
Putting this value of ΔG° in the equation $\Delta G^\circ = -RT \ln K$,

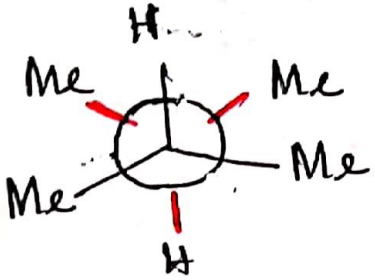
$$\text{we get } K = \frac{(anti)}{(gauche)} = 1{\cdot}9$$

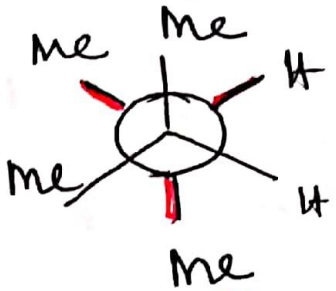
That is, at (25°C) the distribution of conformations in *n*-butane is 66% *anti* and 34% *gauche*.

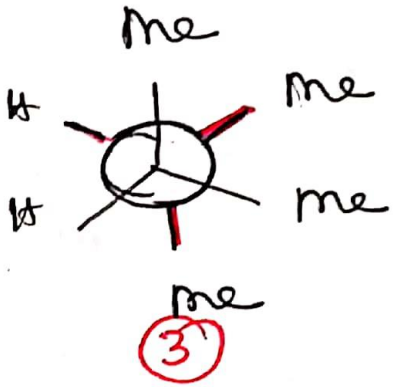
It must be noted that *gauche* conformers of *n*-butane represents chiral molecule but not resolvable for rapid change in conformations.

PE Diagram of 2,3 dimethyl butane









(1) Anti

(2) g⁻

(3) g⁺

(4) Fully eclipsed

(5) Part. Eclipsed

(4) is most. unstable. Fully eclipsed, Steric interaction among similar ligands.

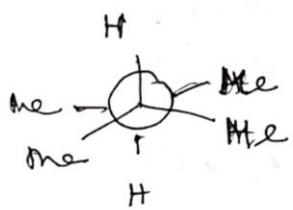
g⁺ & g⁻ are expected to be less stable than anti forms. In g⁺ or g⁻ 3 gauche butane interaction. But in anti forms only two g.b interactions.

But it has been found experimentally that the gauche form and anti form are almost equienergetic

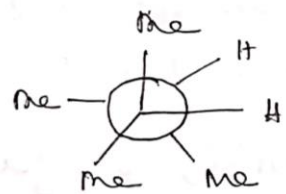
The high stability of gauche form relative to anti form can be explained as:

The $\angle CH_3-C-H$ angle in butane is close to 109°. But due to steric reason the $\angle CH_3-C-CH_3$ angle in 2,3 dimethyl butane is close to 114°.

Thus the ordinary Newmann projection no longer applies. This deformation makes the CH_3 group in anti form to tend towards eclipsed one (V.d.W repulsion increases) But gauche tends towards a CH_3 / CH_3 angle almost 90° (gauche stabilised due to less repulsion).

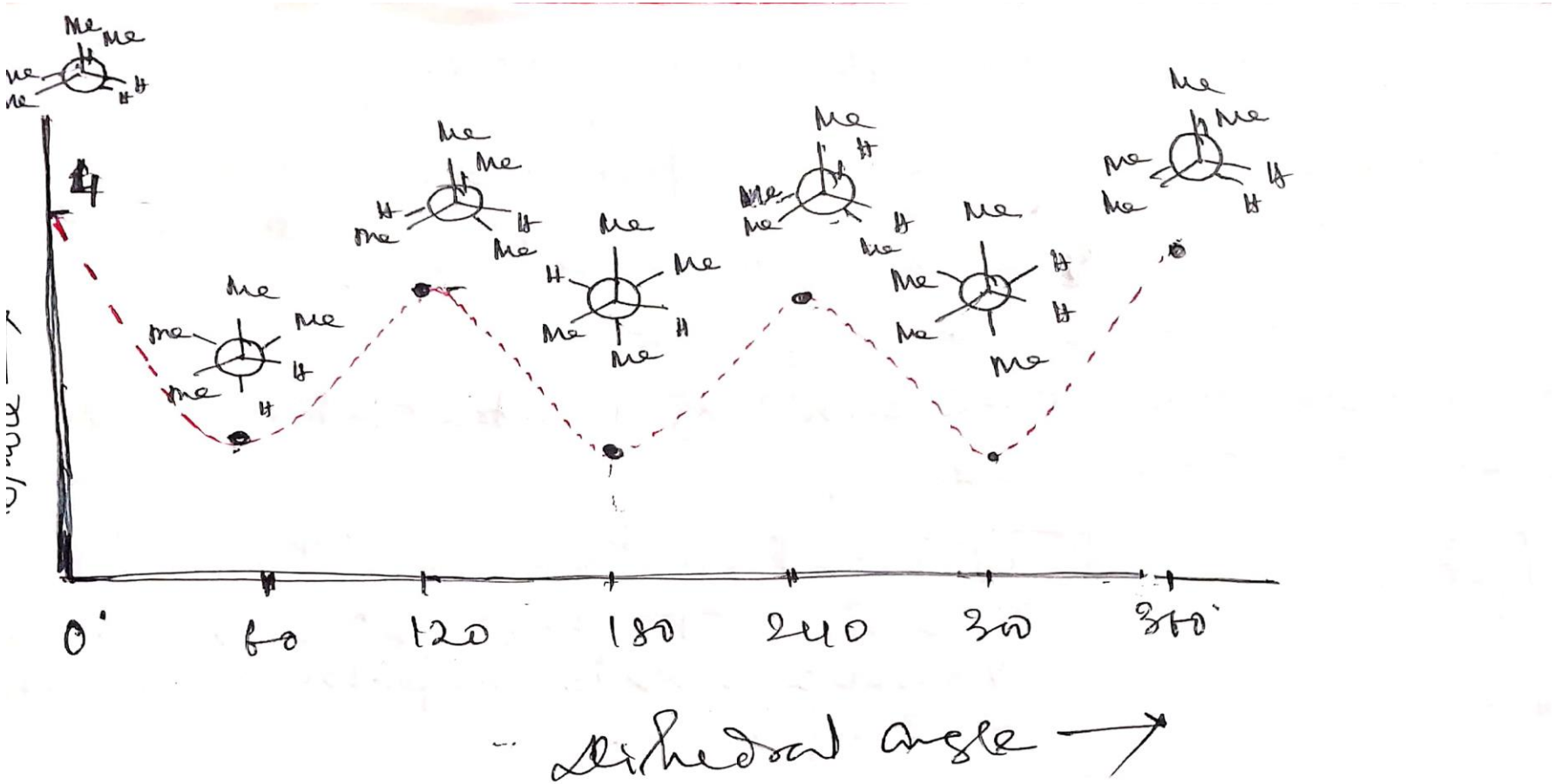


Deformed anti conformer
CH_3/CH_3 interaction increases



Gauche (g-)
CH_3/CH_3 interaction decrease

PE Diagram of 2,3 dimethyl butane

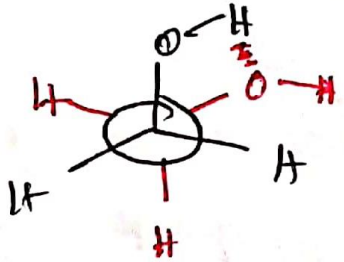


Some H-bonded molecules

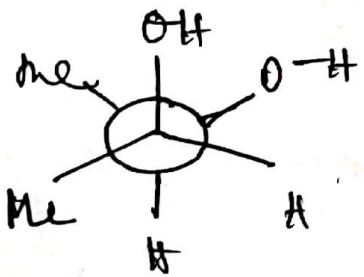
Compounds having general formula CH_2-CH_2 (OH, X) exist mainly in gauche conformations.

X = OH, NH_2, F, Cl, Br, OR, NH_2R etc.

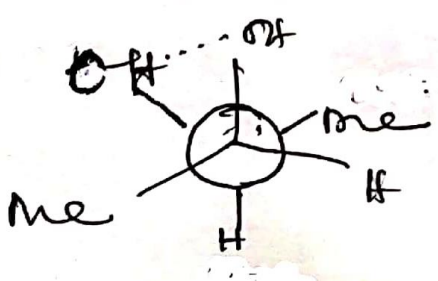
Here stable hydrogen bonding (intramolecular) Stabilise the conformation.



N.B Eclipsed form also form stable H-bond. But torsional strain or Vander waals repulsion destabilise the conformer.



Meso

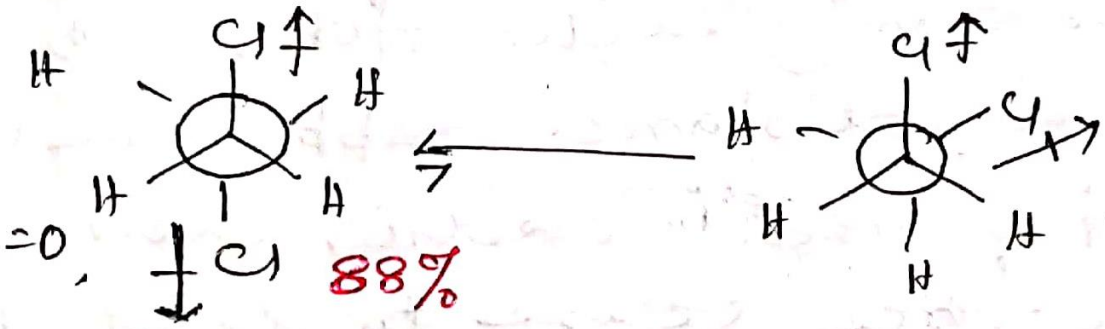


Active

Both meso & active Butane 2,3 diol form intramol H-bond But in Active form methyl groups are anti. So the ratio of bonded to unbonded OH is higher for active than for meso (9)

The dipole moment of CH_2OH-CH_2OH is considerably greater than CH_2Cl-CH_2Cl although $\mu_{C-Cl} \simeq \mu_{C-OH}$ - Why?

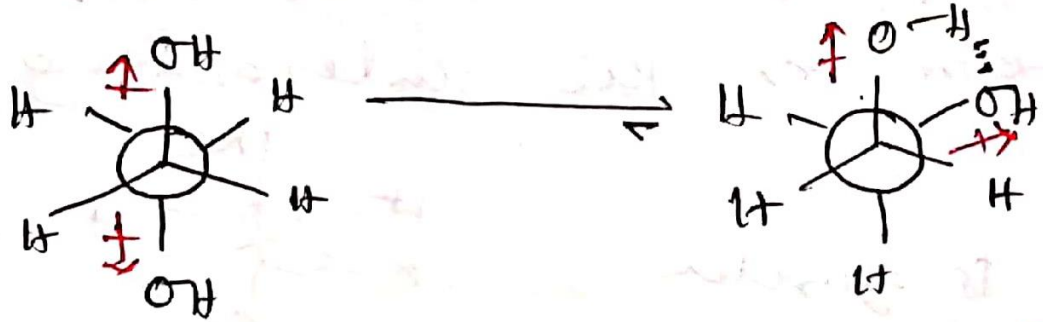
Ans. $\mu^2 = n_a \cdot \mu_a^2 + n_g \cdot \mu_g^2$, Here n_a & n_g are mole fraction of anti & gauche conformers; μ_a & μ_g are dipole moments of anti & gauche forms. μ = dipole moment of the molecule.



$\mu_a = 0$, 88%

μ_g = +ve 12%

$n_a \gg n_g$



$\mu_a = 0$ 1%

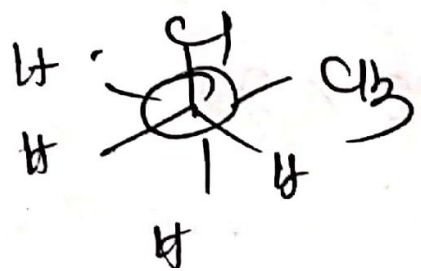
μ_g = +ve 99%

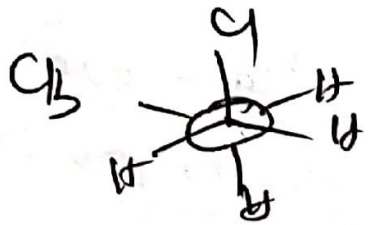
$n_g \gg n_a$

Halolalkanes

Haloalkanes of the type $CH_3-\overset{2}{CH_2}-\overset{1}{CH_2}-Cl$ remains mainly in gauche form (rotation about C_1 C_2 bond) where CH_3 and Cl are in gauche orientation.

Exact reason not known. Possibly, the Vander Waals attractive forces are more than the repulsive force, because in gauche form CH_3 and Cl are separated by a distance approximately the sum of their V.d.W radii, whereas in anti, the attractive force cease to exist due to longer distance between the interacting grps.

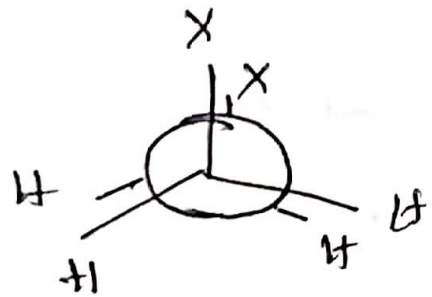




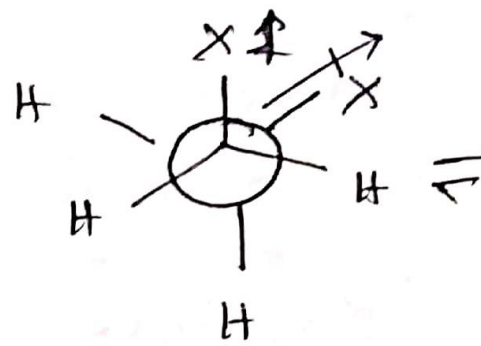
gauche

anti

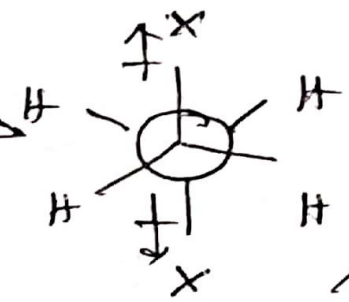
Molecules of the type XCH_2-CH_2-X



Syn



gauche



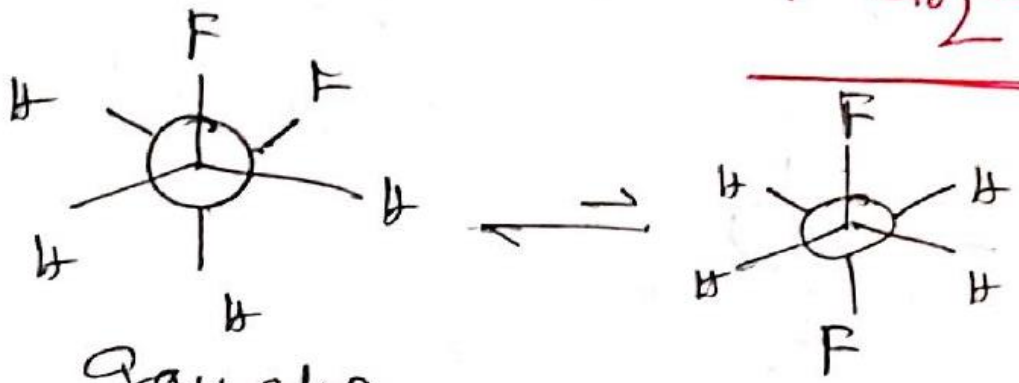
anti

$X = Cl, Br$

- Gauche, less stable; dipolar repulsion.
- Eclipsed, least stable due to steric as well as dipolar repulsion.

* Proportion of gauche increases in polar solvents due to stabilisation of dipolar interactions

FCH_2-CH_2F



Gauche ⇌ Anti

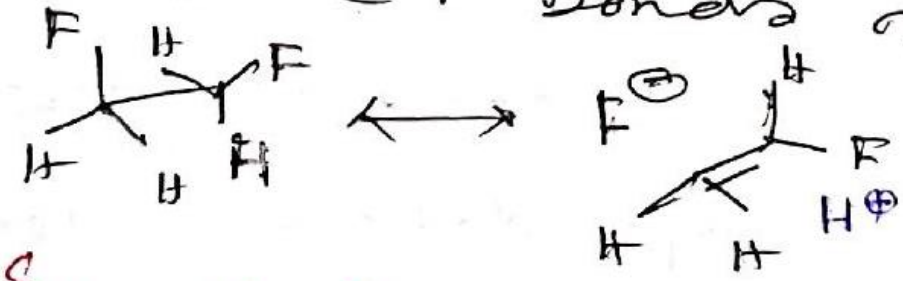
Gauche more stable than Anti even in gaseous state.

Possible explanations:

(1) Allinger et al 1977: Hyperconjugative interaction.

$F-CH_2-CH_2-F \leftrightarrow F^{\ominus}CH=CH-F\,H^{\oplus} \leftrightarrow H^{\oplus}CHF=CH_2F^{\ominus}$

For complete involvement of lone pair of two C–F bonds should be orthogonal,



Small F minimize v.d.w repulsions in gauche form.

Another explanation

Gauche effect, a ~~segment of~~ chain segment A–B–C–D can prefer gauche conformation when A and D are highly electronegative than B or C. or A and D are unshared electron pairs. Here in the example, F are highly electronegative.

Gauche Effect

If a compound contains free electron pairs on adjacent atoms, these electron pairs tend to occupy the skew position to one another. A similar behaviour is exhibited by free electron pairs that are in the vicinity of polar bonds. This phenomenon has come to be known as *gauche* effect. The manifestation of *gauche* effect may be illustrated by the preferred conformations of a few compounds presented below(also see page 272).

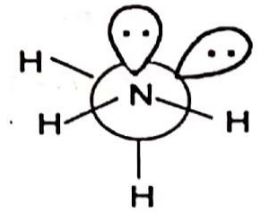
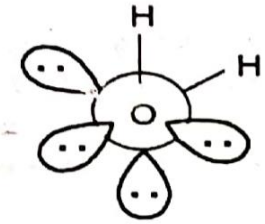
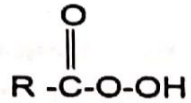
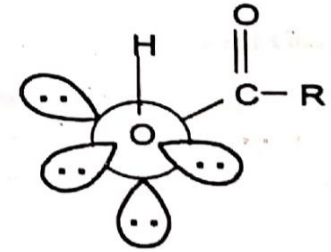
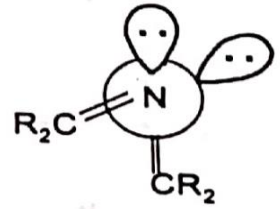
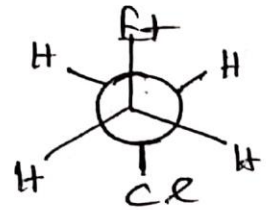
Compound	Formula	Preferred conformation	
Hydrazine	$H_2N\text{-}NH_2$		*P - gauche*
Hydrogen peroxide	HO-OH		*P - gauche*
Peracids			*P - gauche*
Azines	$R_2C{=}N\text{-}N{=}CR_2$		*M - gauche*

Fig. 5. 54

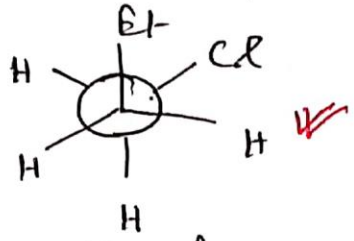
The preference of the *gauche* conformations of 2-haloethanols, 1, 2-dimethoxyethane and related compounds is also interpreted from the stand point of the *gauche* effect in the form of skew interaction of free election pairs with polar bonds. In case of 2-haloethanols, *gauche* effect is further helped by intramolecular H-bonding.

$CH_3-CH_2-CH_2-CH_2-X$, Where X = Cl, Br.

In rotation about C_1/C_2, gauche, more stable.



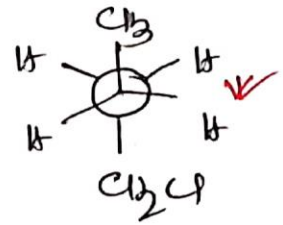
Anti less stable.

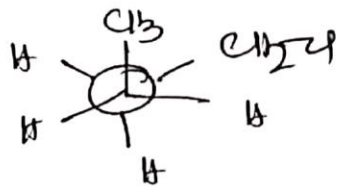


gauche, more stable.

Forces of attractions predominates (between Cl and Cl-)

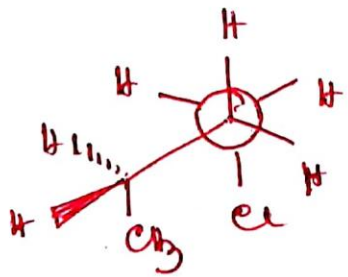
In C_2/C_3 - anti form more stable





Anti more stable - Gauche less stable.

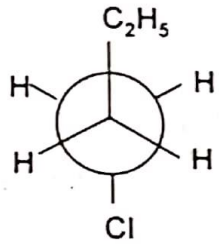
, Forces of repulsion here dominate in gauche form due to bigger size of the groups.



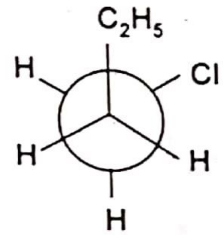
Preferred geometry of gauche

CH_3 and Cl are nearest to each other.

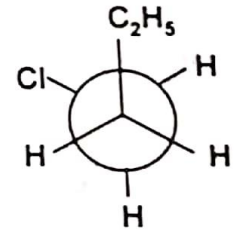
■ $CH_3CH_2CH_2CH_2$-Cl have the following staggered conformations about C-1/C-2 bond.



anti – form



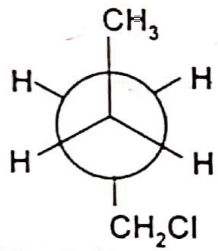
P – *gauche* form



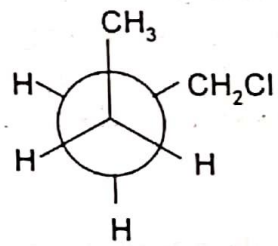
M – *gauche* form

In this case *anti* form is less stable and *gauche* form is more stable by 1.3 kJmol^{-1}. The forces of attraction rather than those of repulsion are operating between the chlorine and ethyl group. The torsion angle in *gauche* form is around 65-70°. It is thought that in this geometry, -C_2H_5 and -Cl are at a distance where van dar Waals attractive forces predominate over the repulsive ones.

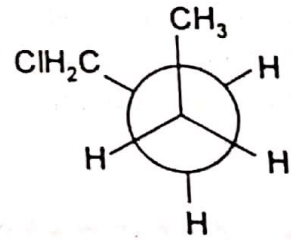
Staggered conformations for rotation about C-2 / C-3 bond are as follows.



anti



P – *gauche*



M – *gauche*

In this case *anti* form is more stable by 1.7 kJ mol^{-1}. In *gauche* forms van dar Waals repulsive forces are predominating because of the bigger size of the groups.