

: Conformational Isomers:

1

Stereoisomers that can be interconverted by the mechanical processes without breaking & making of bonds (chemical process) are known as conformational isomers. Mechanical process includes rotation around single bonds or twisting the bonds. Conformational isomers are also known as rotamers or rotational isomers.

Conformational isomers or conformers require 16-25 kJ mole^{-1} energy for interconversion & that is why they are not isolable under ordinary temperature. Each conformation will have different energy & the lower energy conformation will be populated in preference to those of higher energy. When the molecule has a number of conformations that corresponds to energy minima then they are called conformers.

Different strains present in a molecule.

Different strains (applicable for cyclic molecule).

Size of Ring	Angle strain (deviation from $109^\circ 28'$)
3	$24^\circ 44'$ [$= \frac{109^\circ 28' - 60^\circ}{2} = 24^\circ 44'$].
4	$9^\circ 44'$ [$= \frac{109^\circ 28' - 90^\circ}{2} = 9^\circ 44'$]
5	$0^\circ 44'$
6	$-5^\circ 16'$ [$= \frac{109^\circ 28' - 108^\circ}{2} = 0^\circ 44'$].

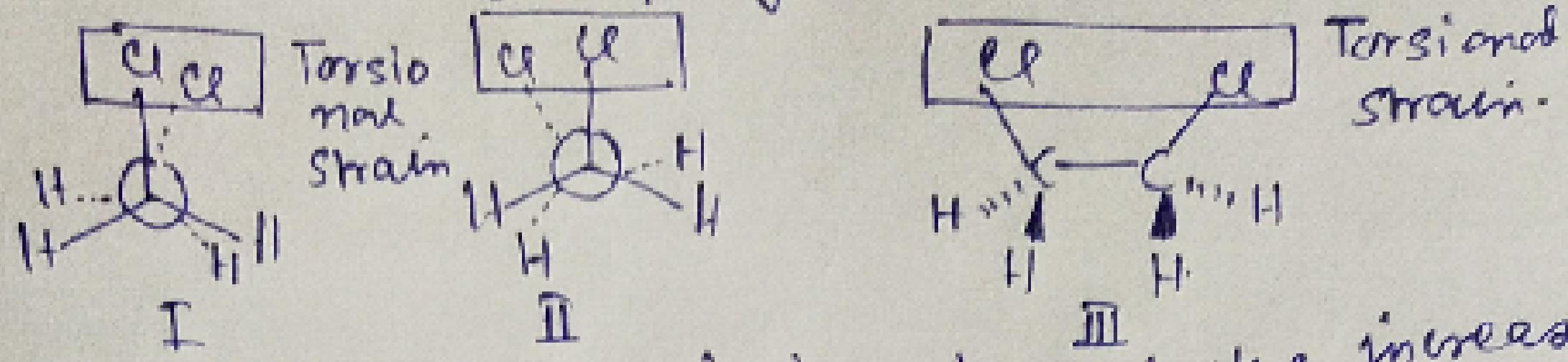
Considering only angle strain

3 7 4 7 6 7 5.

$$\left[= \frac{109^\circ 28' - 120^\circ}{2} = -5^\circ 16' \right].$$

B. Torsional strain (Eclipsing strain)

2



Torsional strain or eclipsing strain is the increase in potential energy of a molecule due to repulsion between electrons in bonds that do not share an atom. Consider two

C. Steric strain (Vanderwaals strain):

When two nonbonded atoms or groups are separated by the sum of their Vanderwaals radii, their mutual repulsion is maximum. The repulsion between the electrons clouds on the different nonbonded atoms is the essence of Vanderwaals strain. More atoms is the size of atoms or groups, more will be steric strain.

Different conformations of ethane with different dihedral angle. first let us define the dihedral angle.

Dihedral angle is defined as angle between two intersecting planes.

The dihedral angle of a molecule

AC-C-B is the dihedral angle = 180° .

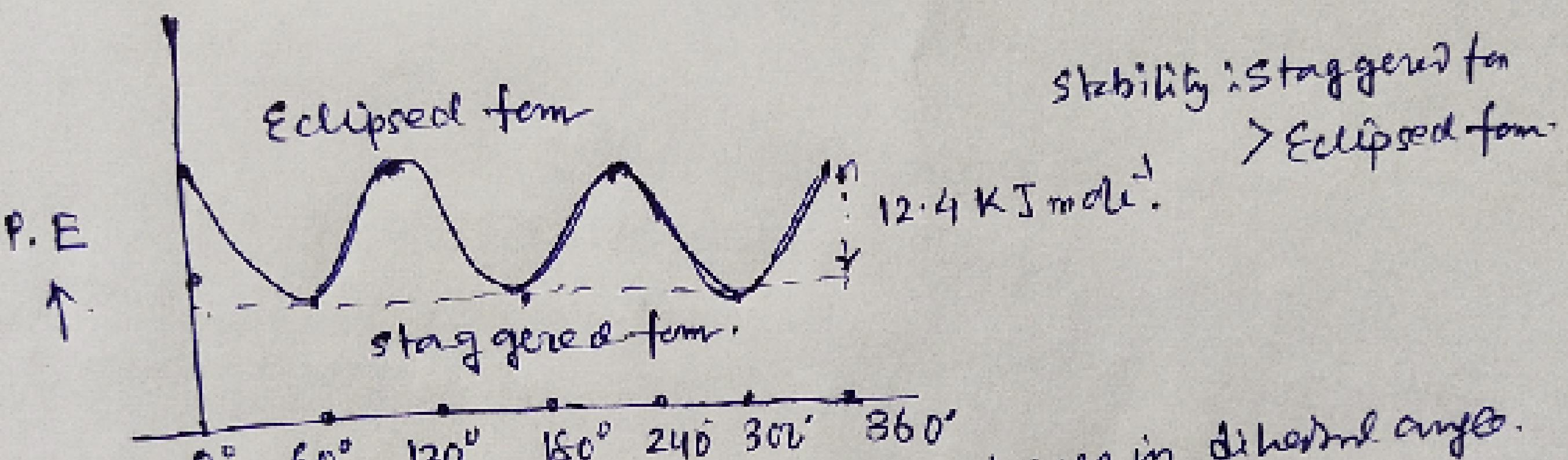
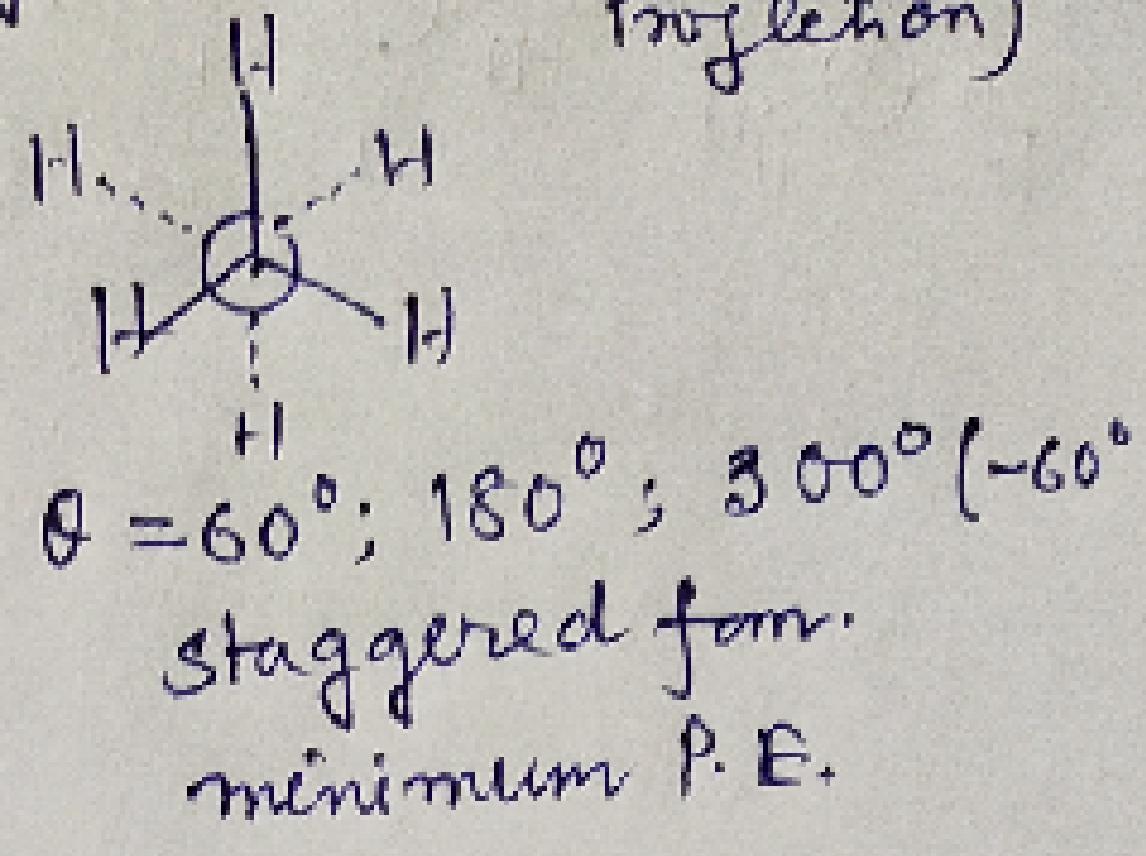
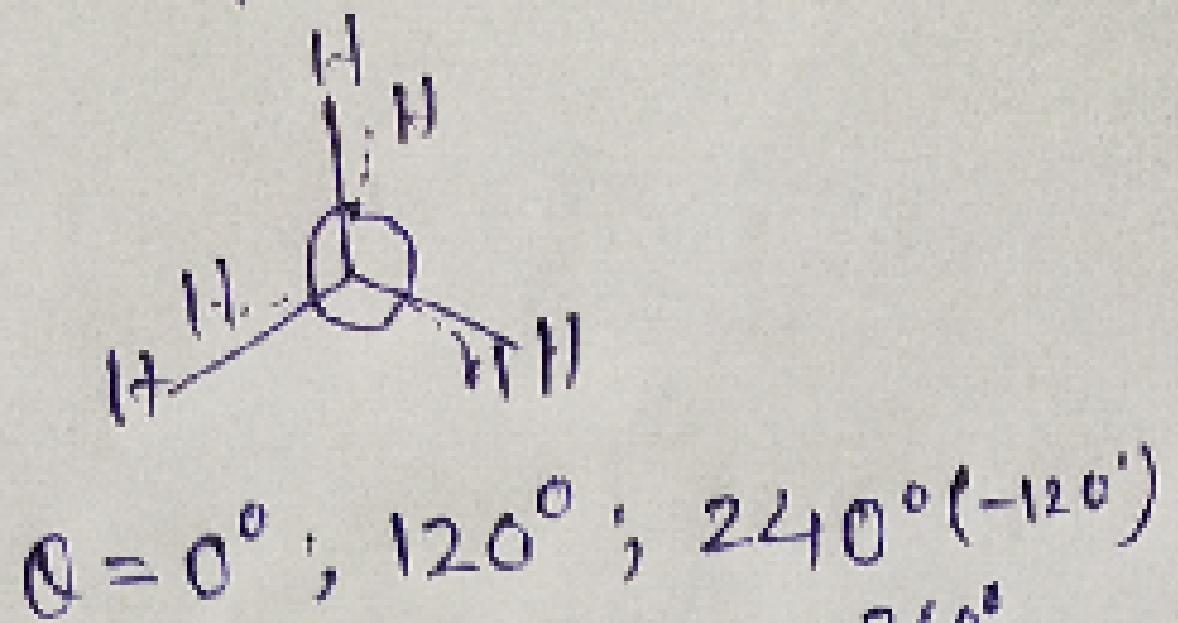
AC-C-B is the dihedral angle = 0° .

The dihedral angle between planes ACC & CCB as shown above.

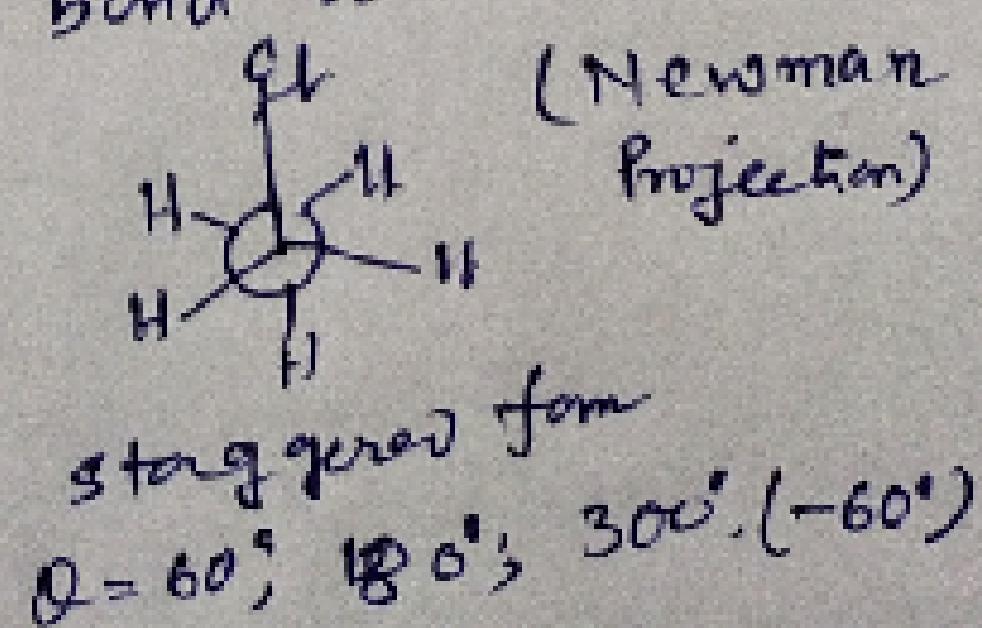
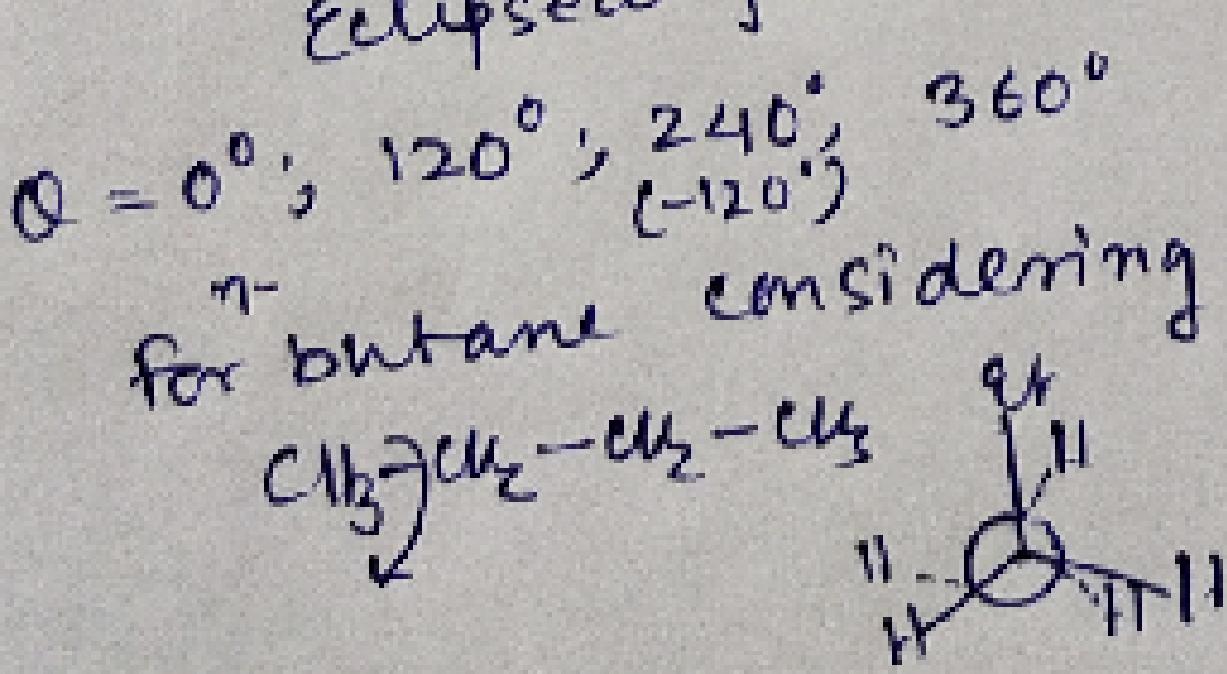
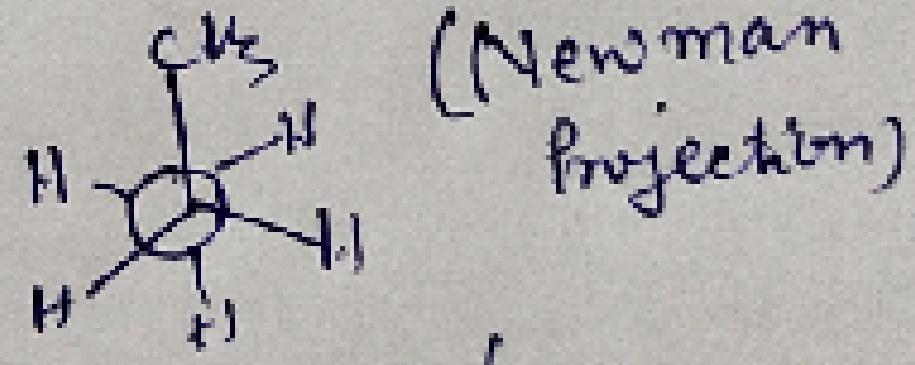
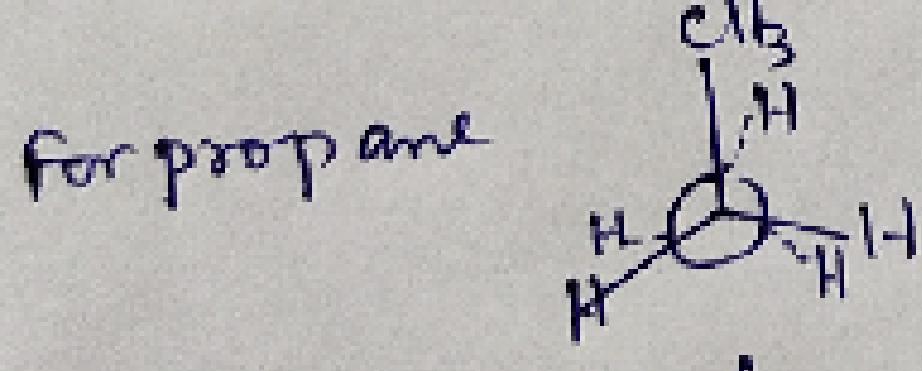
dihedral angle = 60° .

3

Conformational isomer of ethane (Newman projection)

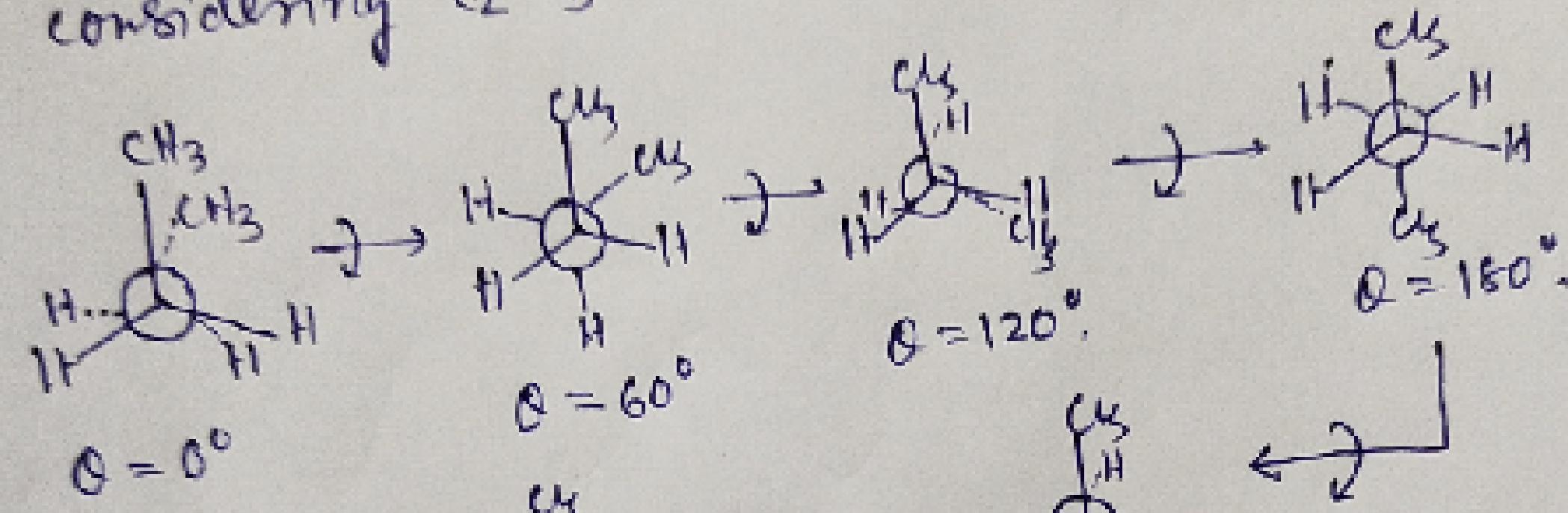


Potential energy change with change in dihedral angle.
 \Rightarrow At 25°C , there is only one molecule of staggered ethane for each one hundred & sixty of staggered ethane i.e. population of eclipsed ethane is negligible.



The same energy diagram is observed. The only difference is energy barrier between eclipsed & staggered form ④ is higher i.e. 14.2 kJ mol^{-1} for propane & 16.8 kJ mol^{-1} .

Torsional curve (Energy diagram) for n-butane considering C_2-C_3 bond rotation: $C_1H_3-C_2H_2 \rightleftharpoons C_2H_2-C_3H_3$



(Newman projection)
 $\theta = 0^\circ$; fully eclipsed form.
 $\theta = 120^\circ$ or $\theta = 240^\circ (-120^\circ)$; partially eclipsed form.

$\theta = 180^\circ$; Anti or fully staggered form.

$\theta = 60^\circ / 300^\circ / -60^\circ$; Partially staggered form or gauche form.

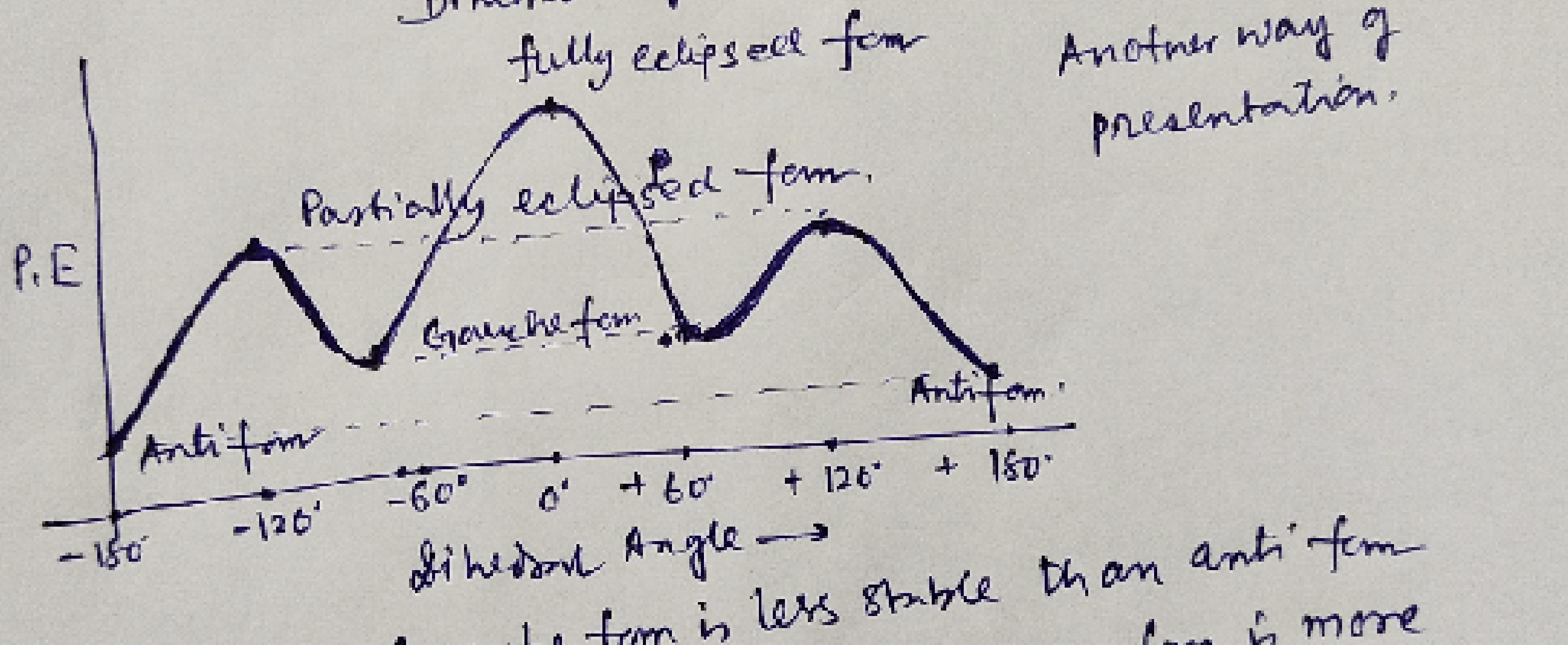
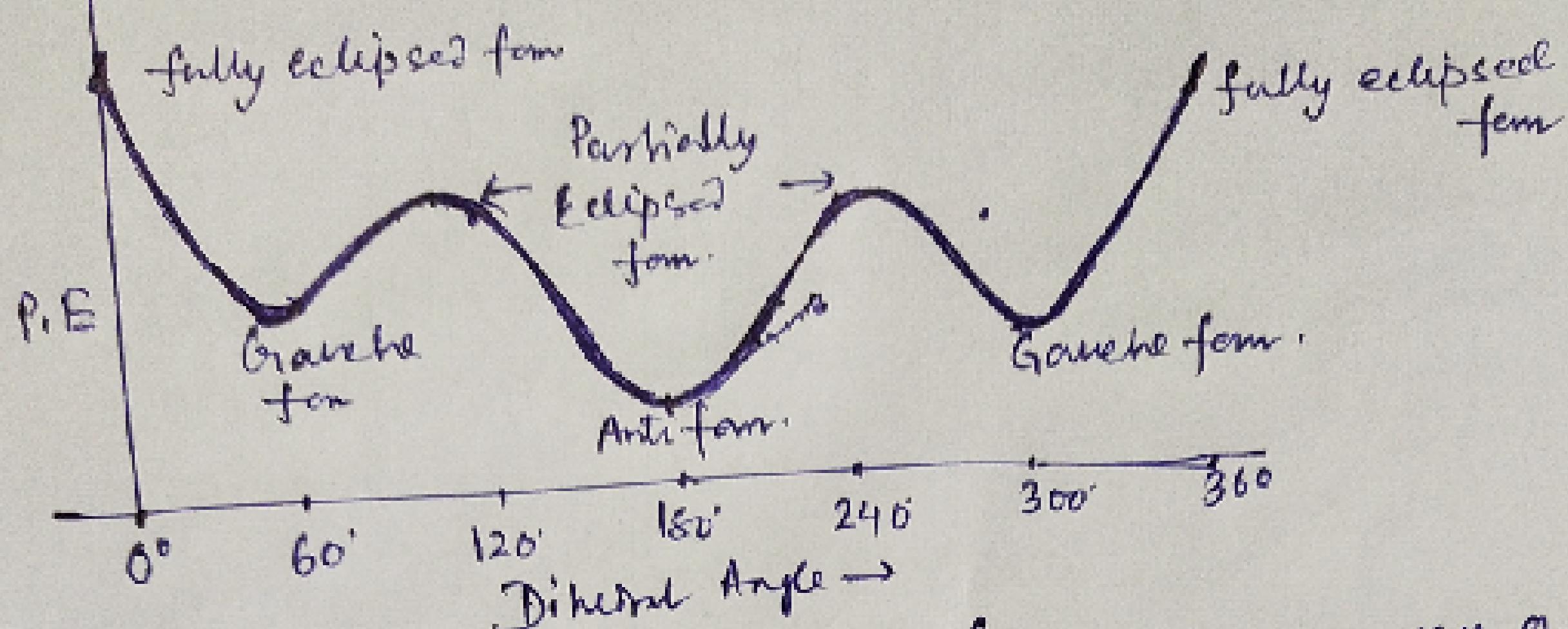
Stability order:
Anti form $>$ Gauche form $>$ Partially eclipsed form
 $>$ fully eclipsed form.

P.E order: Reverse:

\Rightarrow Torsional strain or steric strain is ~~max~~ maximum in fully eclipsed form & zero at anti-form.

\Rightarrow The energy difference between gauche & anti form is phase dependent.

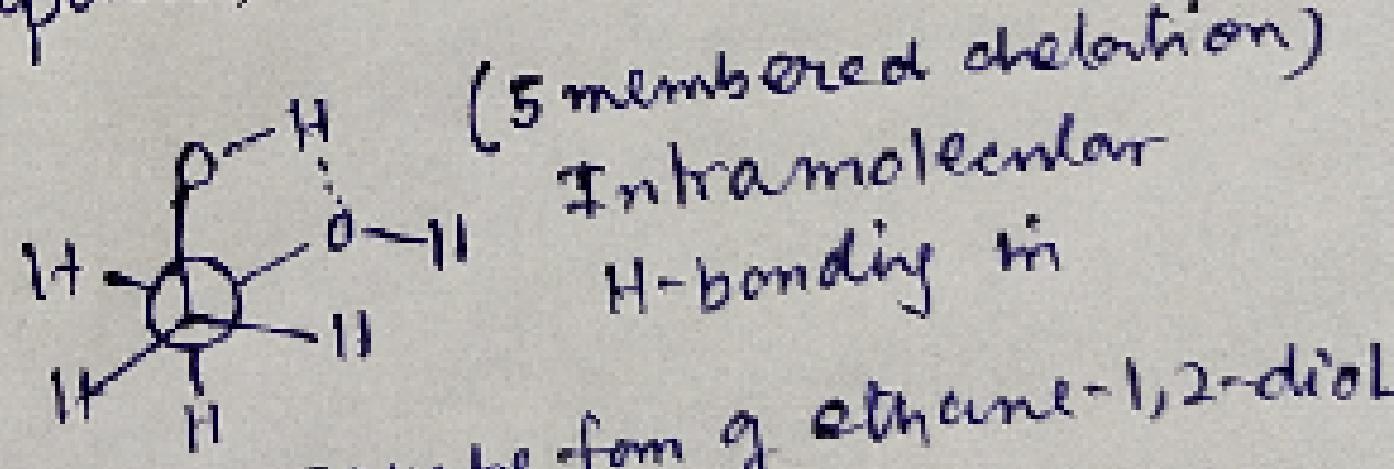
(5)



Another way of presentation.

Generally Brachе form is less stable than anti-form but for following compounds Brachе form is more stable than anti-form.

a) 2-fluoro ethanol.



b) 2-nitro ethanol.

gauche form of ethane-1,2-diol makes gauche form more stable

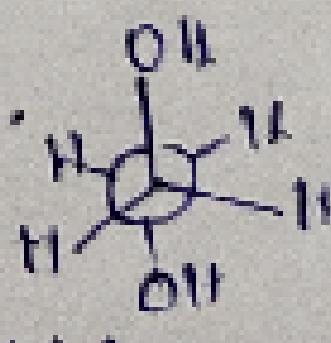
c) 2-amino ethanol.

than anti-form when there

d) Ethylene glycol

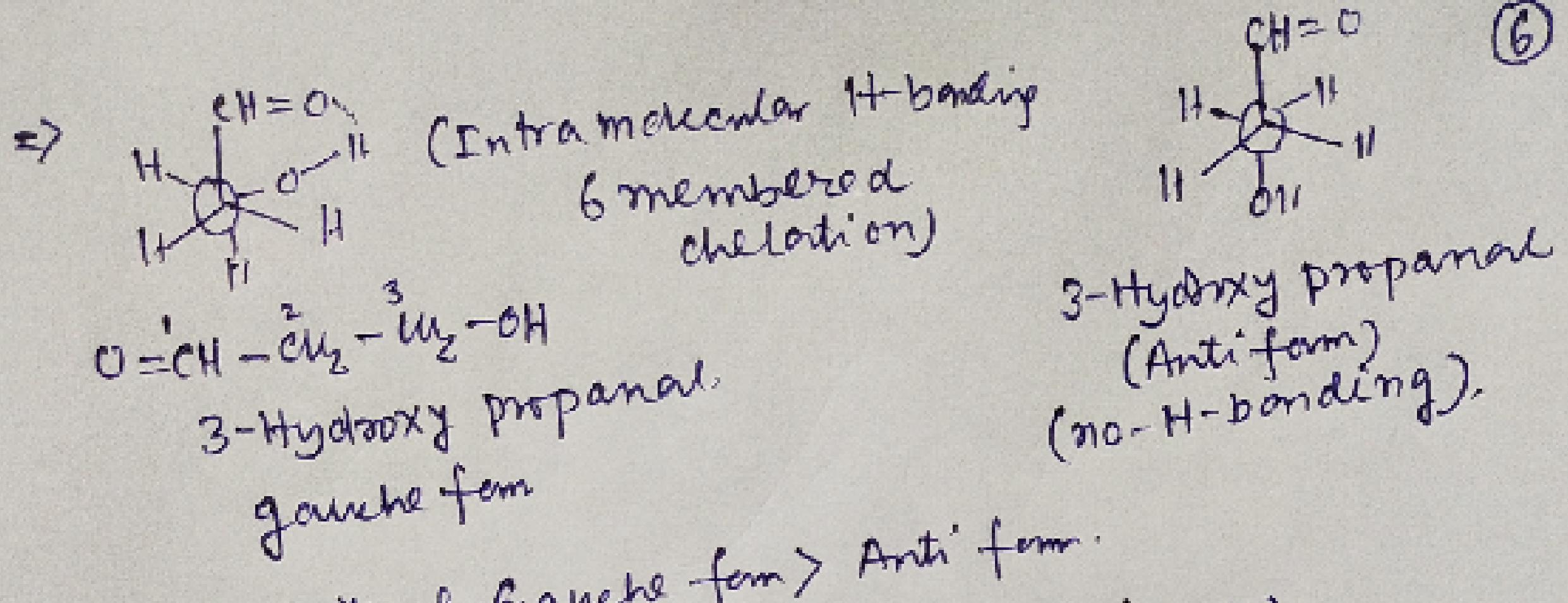
is no H-bonding.

or
Ethane-1,2-diol.



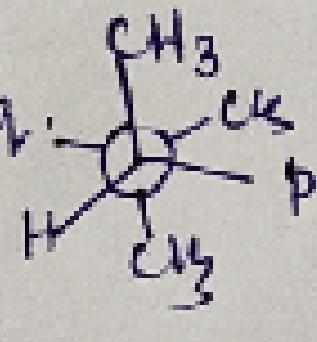
e) 3-Hydroxy propanoic acid.

f) 3-Methoxy propanoic acid.

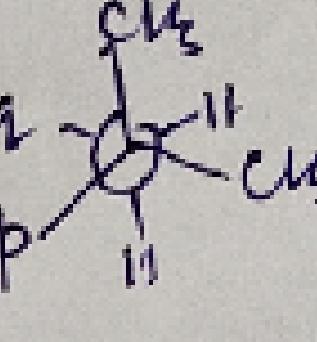


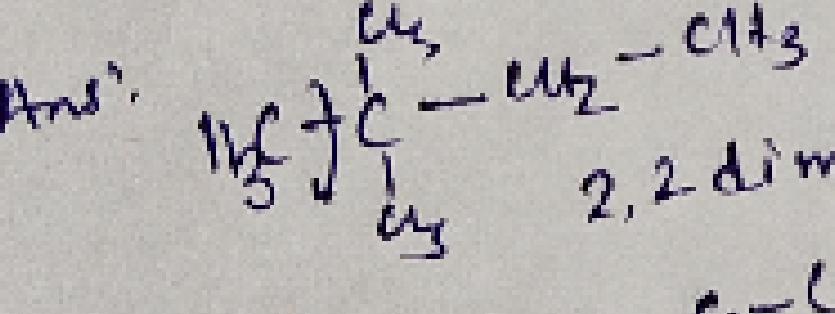
\Rightarrow Stability of Gauche form > Anti form.

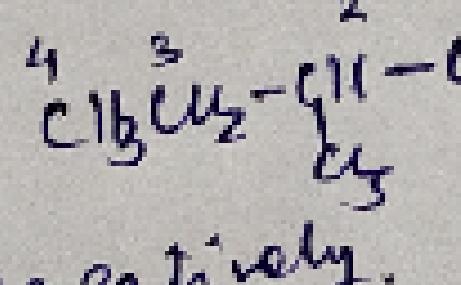
Questions: (Based on conformational isomer)

Q1. for 2,3 dimethyl butane, the conformational isomer is given as follows. a.  find p & q.

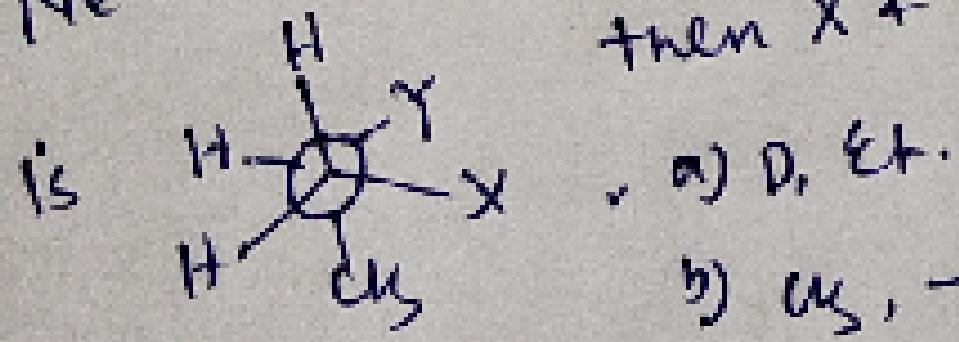
Ans: $p = -\text{CH}_3$; $q = -\text{H}$.

Q2. for 2,2-dimethyl butane, the conformational isomer is given as follows. a. 

Ans.  2,2-dimethyl butane.
 Considering C_1-C_2 bond rotation; $q = -\text{H}$, $p = -C_2\text{H}_5$.
 Considering C_2-C_3 bond rotation; $p \rightarrow -\text{CH}_3$; $q = -\text{CH}_3$.

Q3 Newman projection representation of 

then X & Y may be respectively.



c) $-\text{CH}_2\text{D}_2$; $-\text{CH}_3$

d) $-\text{CH}_3$; $-\text{CH}_2\text{D}$.

Considering C_1-C_2 bond rotation, $X \Rightarrow -\text{D}$; $Y \Rightarrow -\text{Et}$.
 Considering C_2-C_3 bond rotation, $X \Rightarrow -\text{CH}_3$; $Y \Rightarrow -\text{CH}_2\text{D}$.

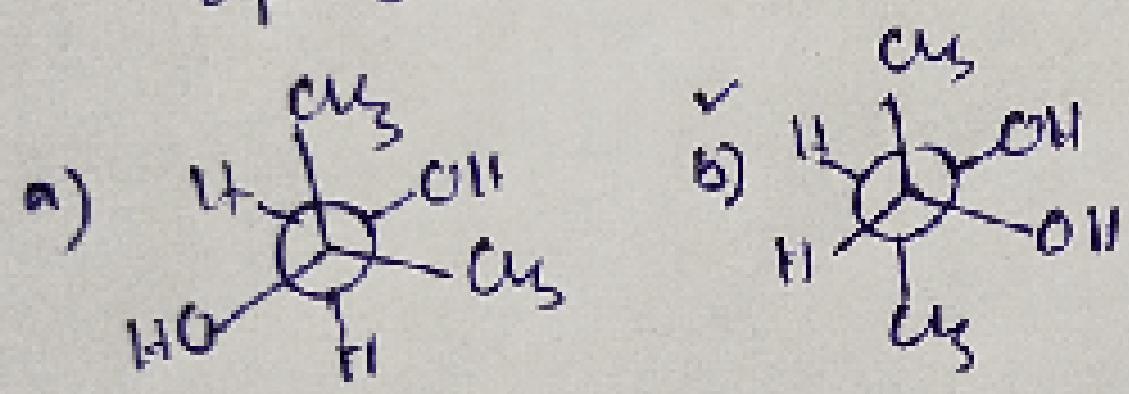
Q. 4. Most stable conformation of ethane 1,2 diol in H_2O is (7)

- a) Gauche b) Anti c) Ellipsed (fully) d) Partially eclipsed.

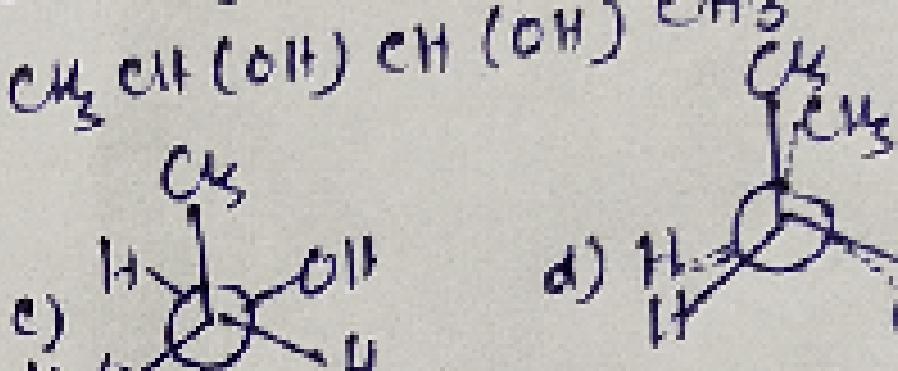
Q. 5. On increasing temperature, the dipole moment of 1,2 dichloro ethane (1) remains (2) same (3) can not be decided.

- a) increases b) decreases

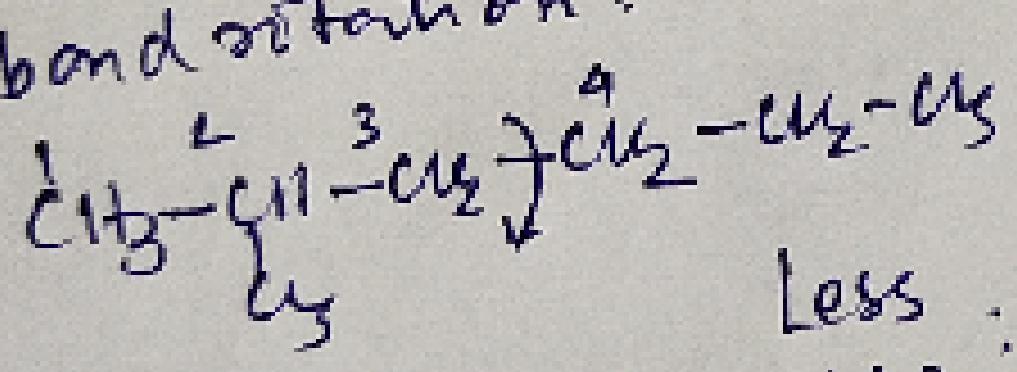
Q. 6. What is the most stable form for C_2-C_3 rotation of Butane 2,3 diol.



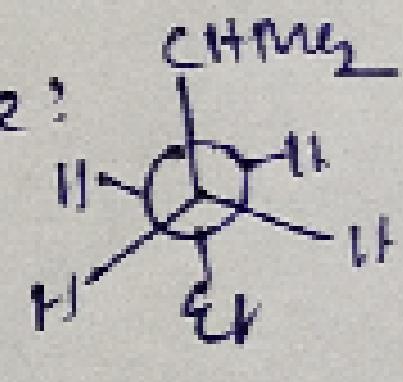
c)



Q. 7. What is the most stable & least stable conformation for 2-methyl hexane considering C_3-C_4 bond rotation?



Ans: Most stable: Isopropyl

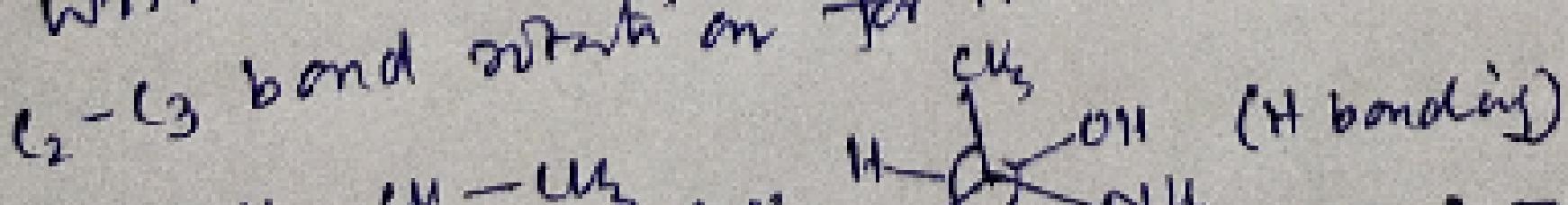


Less stable:

Q. 8. For which molecule, Gauche conformer is more stable than anti conformer.

- a) CH_2-CH_2 b) CH_2-CH_2 c) CH_2-CH_2 d) CH_2-CH_2

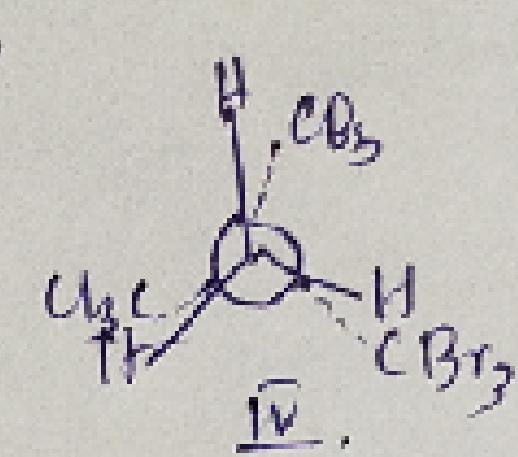
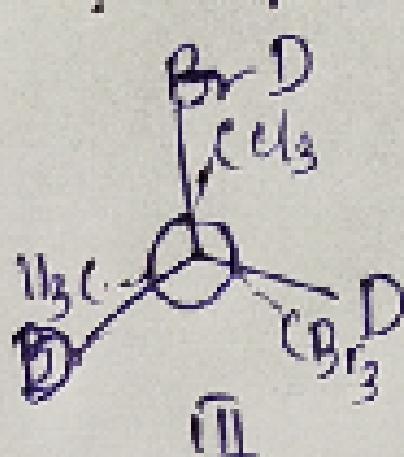
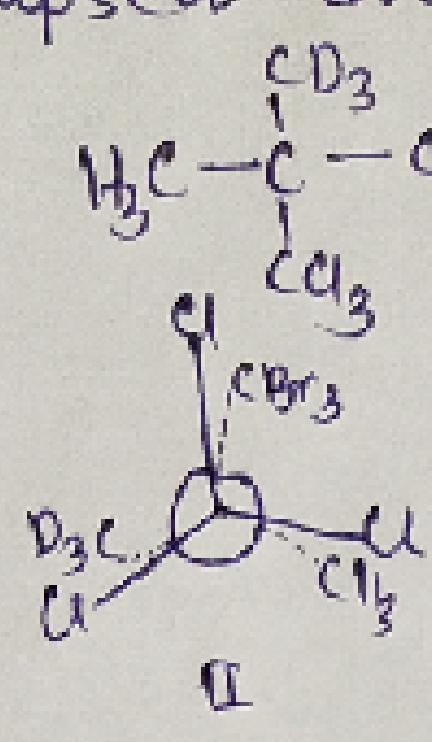
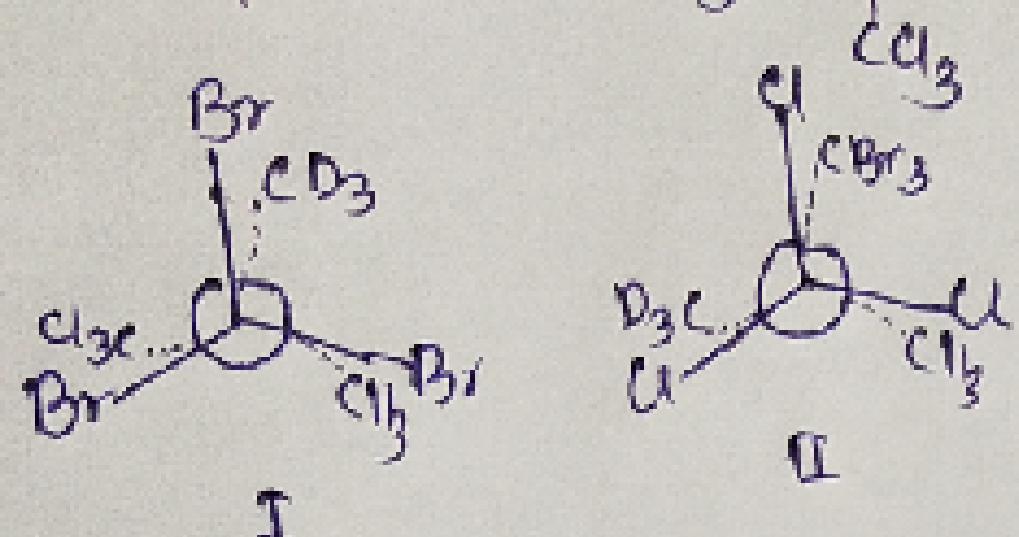
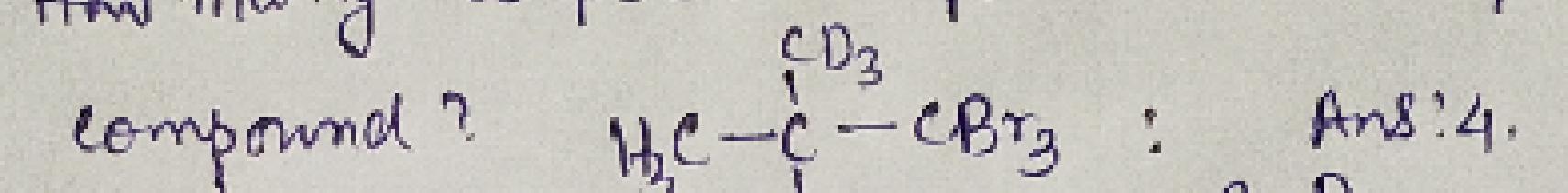
Q. 9. Write down the most stable conformer around C_2-C_3 bond rotation for the molecule 3-Amino-2-butanol.



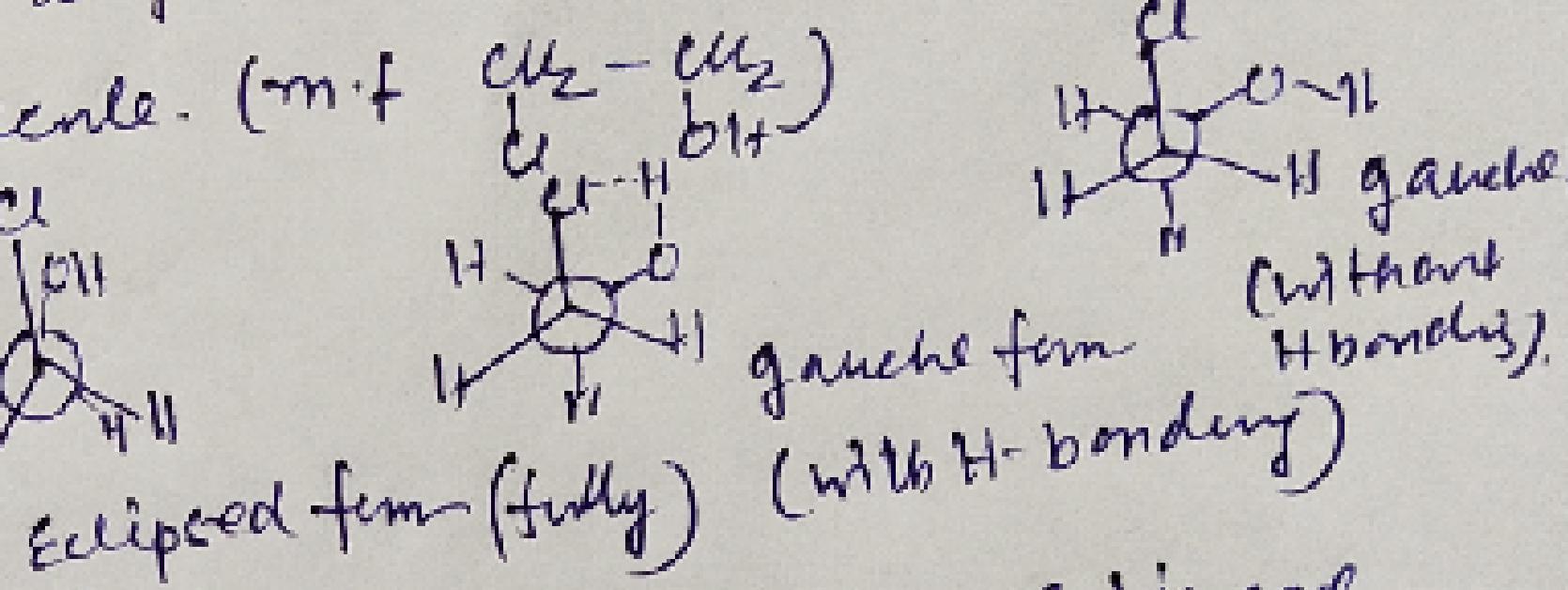
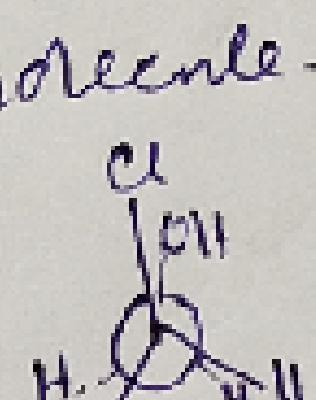
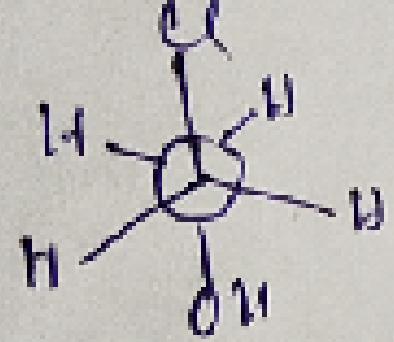
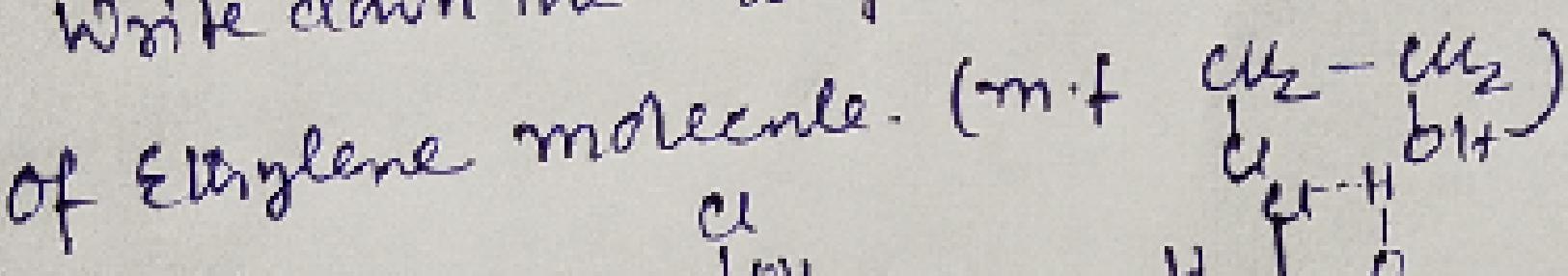
$\text{OH} \quad \text{NH}_2$ $\text{CH}_3-\text{CH}_2-\text{CH}_2+\text{CH}_3$ at

anti-form, steric repulsion is least.

Q. How many eclipsed conformations are possible for the compound? $\text{H}_3\text{C}-\overset{\text{CD}_3}{\underset{\text{Br}}{\text{C}}} - \text{CBr}_3$: Ans: 4. (8)



Q. 11. Write down the conformational isomers of chlorohydrin of Ethylene molecule. (m.f $\text{CH}_2-\text{CH}_2\text{OH}$)

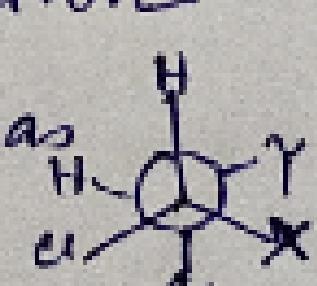


Stability order : Gauche form > Anti-form > Eclipsed form (with H-bonding)

Eclipsed conformation of ethylene chlorohydrin provides the most favourable condition for the formation of intramolecular hydrogen bond due to closer disposition of interacting $-\text{OH}$ & $-\text{Cl}$ groups. But steric hindrance along with dipole-dipole repulsion makes the eclipsed conformation most unfavorable/unstable.

Q. 12 For the compound $\text{CH}_3-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{CH}}} - \text{CH}(\text{Br}) - \text{CH}_3$. The given Newman projections can be represented as

Find the value of X & Y.



a) $-\text{CH}_3$; $-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{CH}}}-\text{Br}$

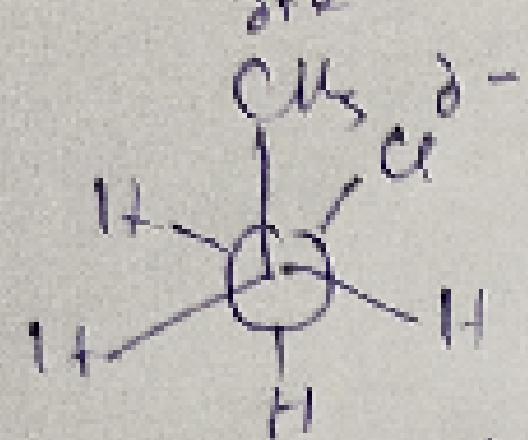
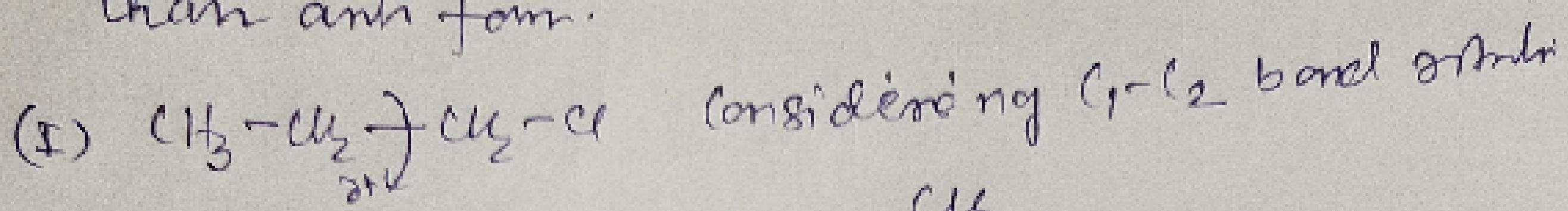
b) $-\text{CH}_3$; $-\text{CH}_3$.

c) $-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{CH}}}-\text{CH}_3$; $-\text{CH}_2\text{Br}$

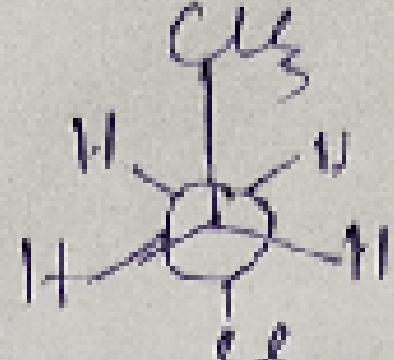
d) $-\text{CH}_2\text{Cl}$; $-\text{Br}$.

e) $-\text{CH}_2-\text{CH}_3$; $-\text{CH}_2\text{Br}$

Other factors where gauche form is more stable than anti-form.

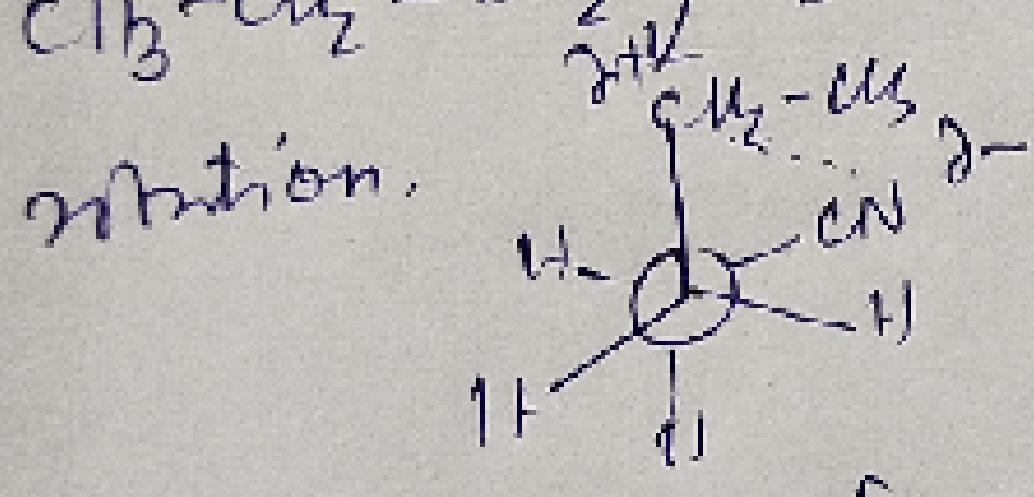
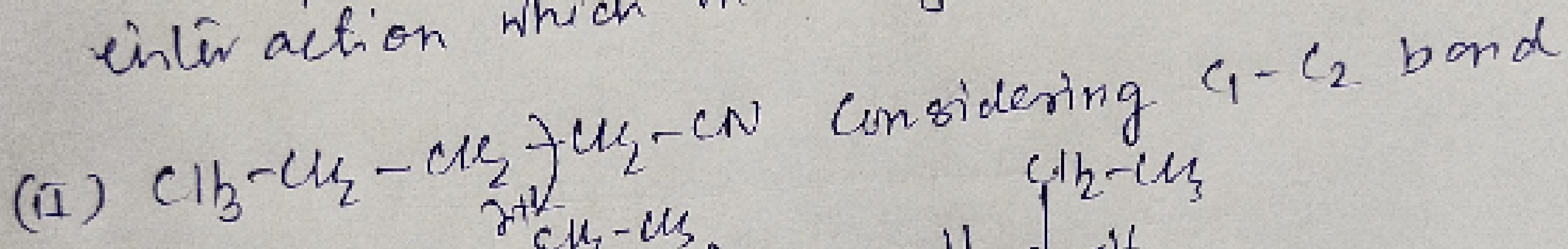


gauche form

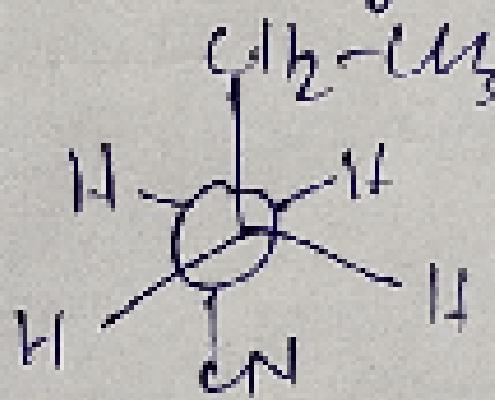


anti-form

In Gauche form, $-\text{Cl}$ develops $\delta-$ charge & $-\text{CH}_3$ develops $\delta+$ charge & there is dipole-dipole interaction which makes Gauche form more stable.

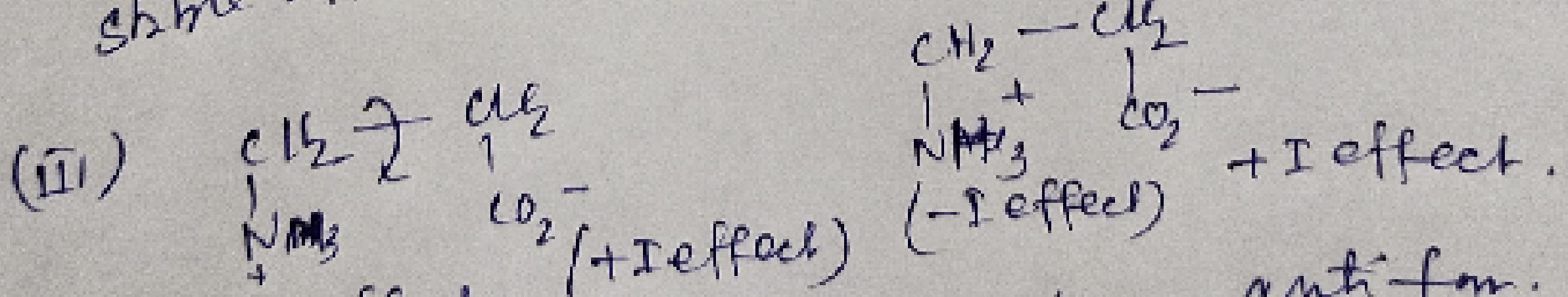


gauche form



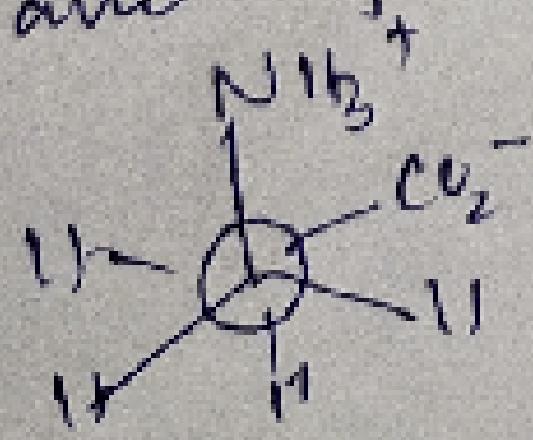
Anti-form

for the same reason again Gauche form is more stable than anti-form.

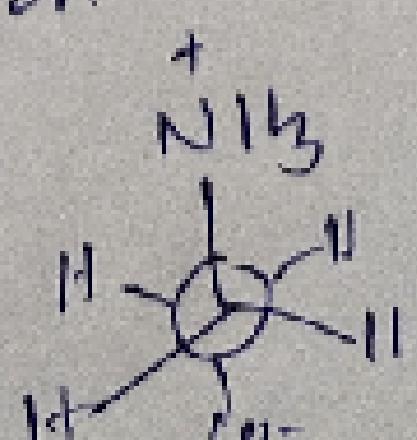


(-I effect)

Gauche form is more stable than anti-form.



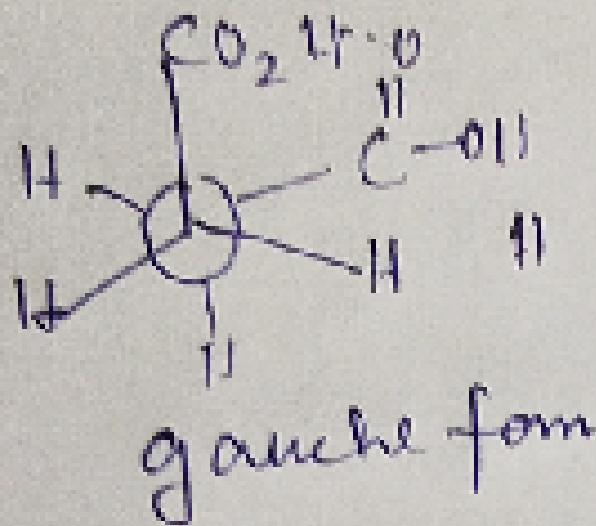
due to ion-ion interaction.



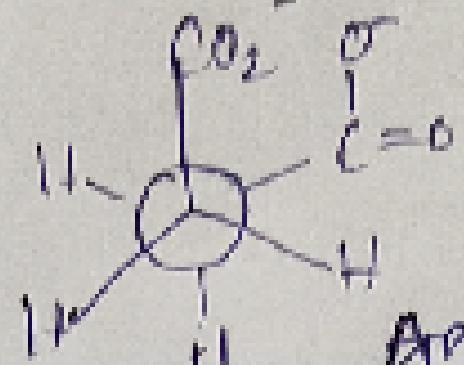
Ion-Ion interaction is not possible in anti-form.

10

Q. Succinic acid. Gauche form is more stable than anti-form. But at very high pH [OH concentration is high]. anti-form is more stable than gauche form.



gauche form.



gauche form of succinic acid at very high pH.
pH = 14.

H bonding is possible in gauche form which makes it more stable.

Ion-Ion repulsion takes place in gauche form which makes it less stable.

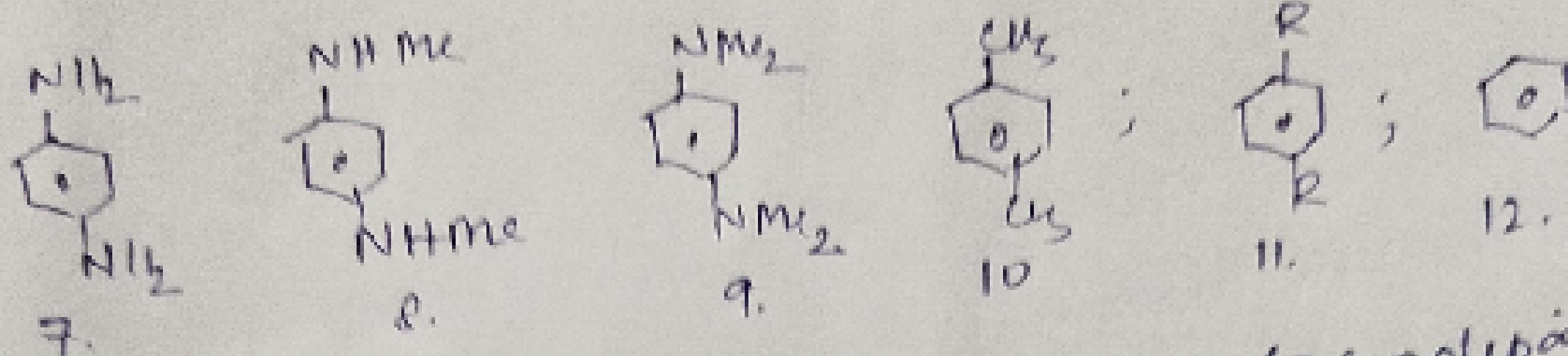
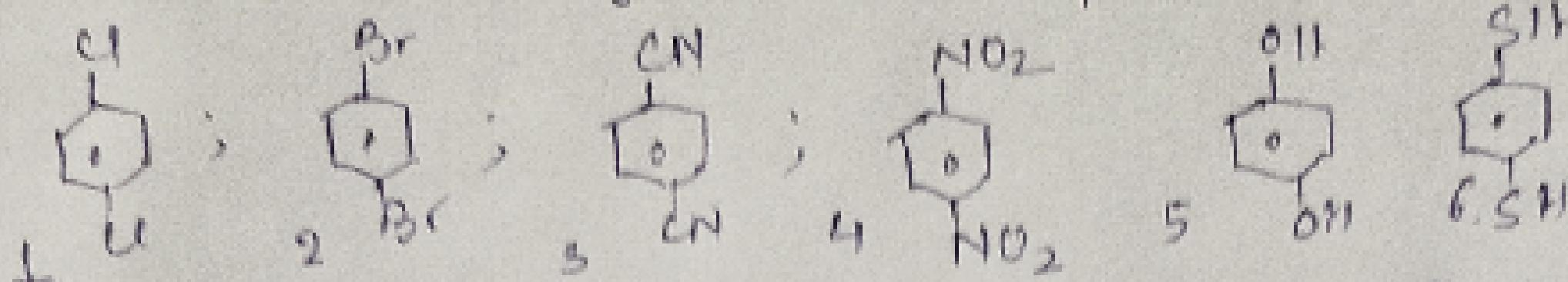
Q. $\text{CH}_3-\overset{2}{\text{CH}}-\overset{1}{\text{CH}}-\overset{3}{\text{CH}}-\text{Cl}$
Considering C_1-C_2 bond rotation: Stability Gauche > Anti
Considering C_2-C_3 bond rotation: Stability Anti > Gauche.
Considering C_1-C_2 bond rotation

dipole-dipole interaction makes gauche form more stable.
Considering C_2-C_3 bond rotation

repulsion makes gauche form more stable than anti form.

Q.
correct option regarding compound.
a) Given conformer has zero dipole moment
b) (not giving positional isomer with 1,2 dichloro benzene).
c) Net dipole of cpd(1mole) is nonzero.
d) Don is even

Q. Dipole moment of which compound is zero. 11



Ans: 1, 2, 3, 4, 10, 11, 12. (zero dipole moment)



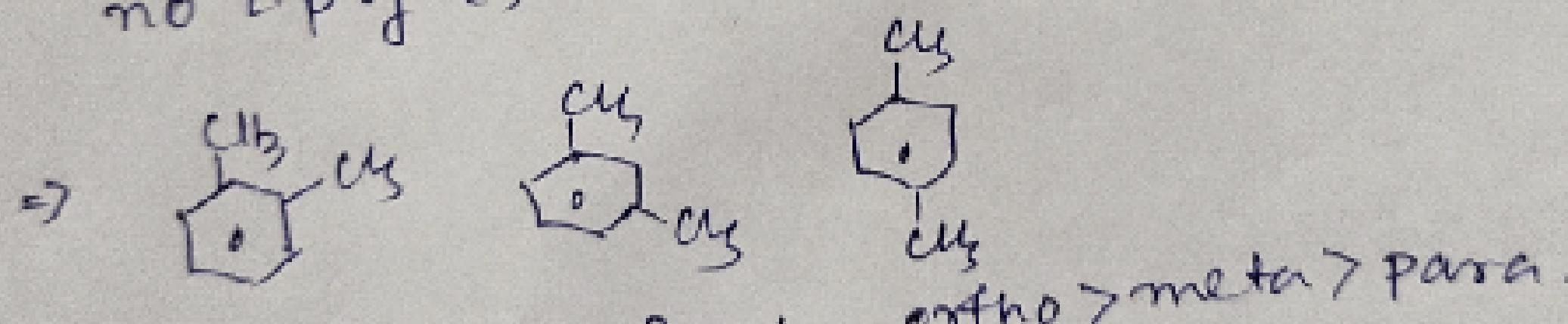
6, 7, 8, 9, 10, 13 (nonzero dipole moment)

⇒ For linear grp. net dipole moment is zero.

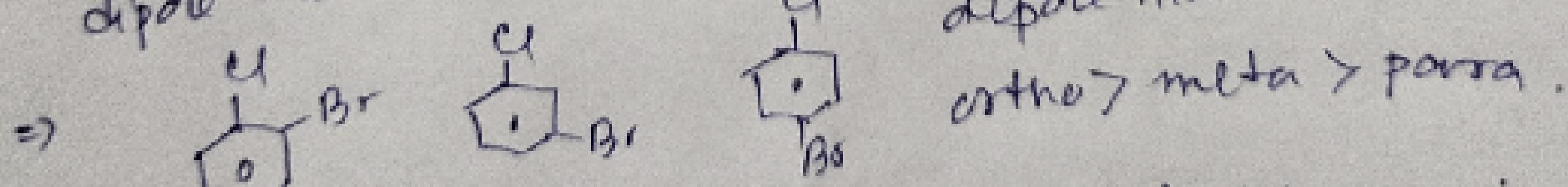
⇒ For nonlinear grp. with central atom has atleast 2 p g e, then net dipole moment is nonzero.

⇒ For nonlinear grp. with central atom has no 2 p g e, then net dipole moment is zero.

⇒ For nonlinear grp. with central atom has no 2 p g e, then net dipole moment is zero.

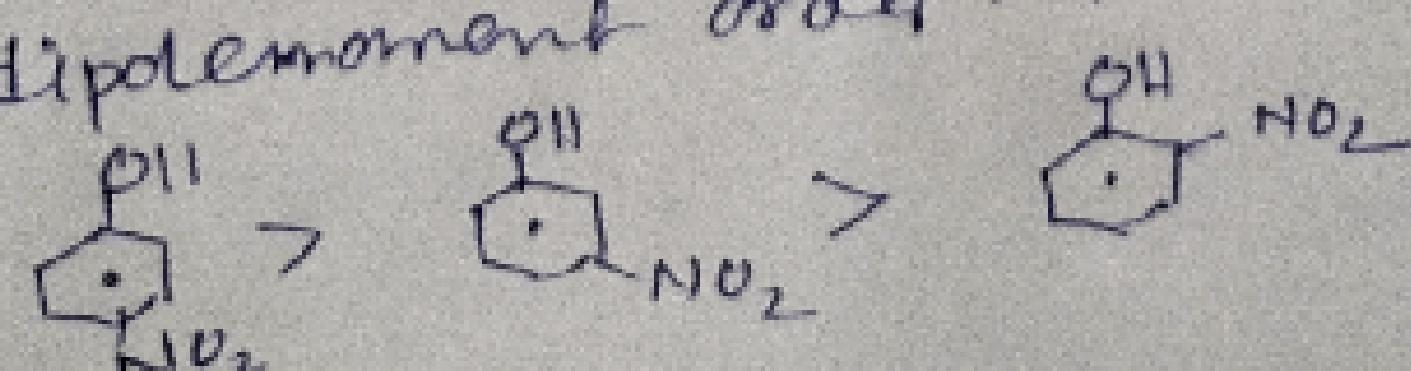


dipole moment order:

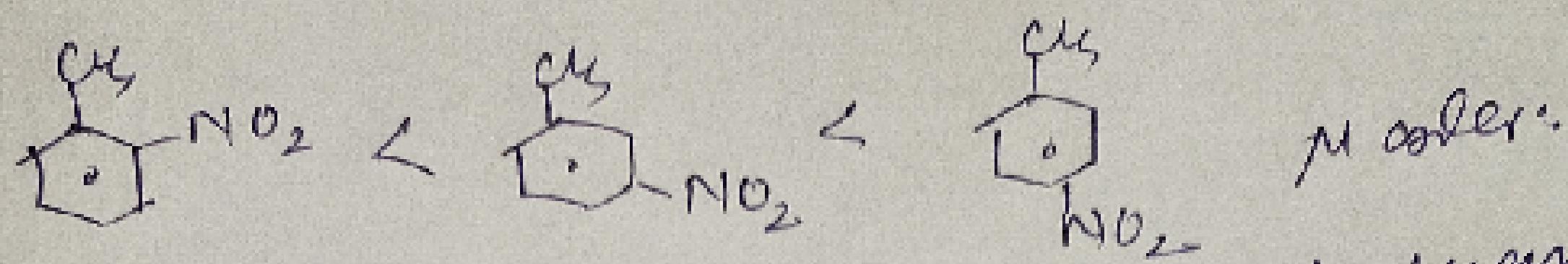


⇒ If groups having different effect, one is EDG & another is EWA, then

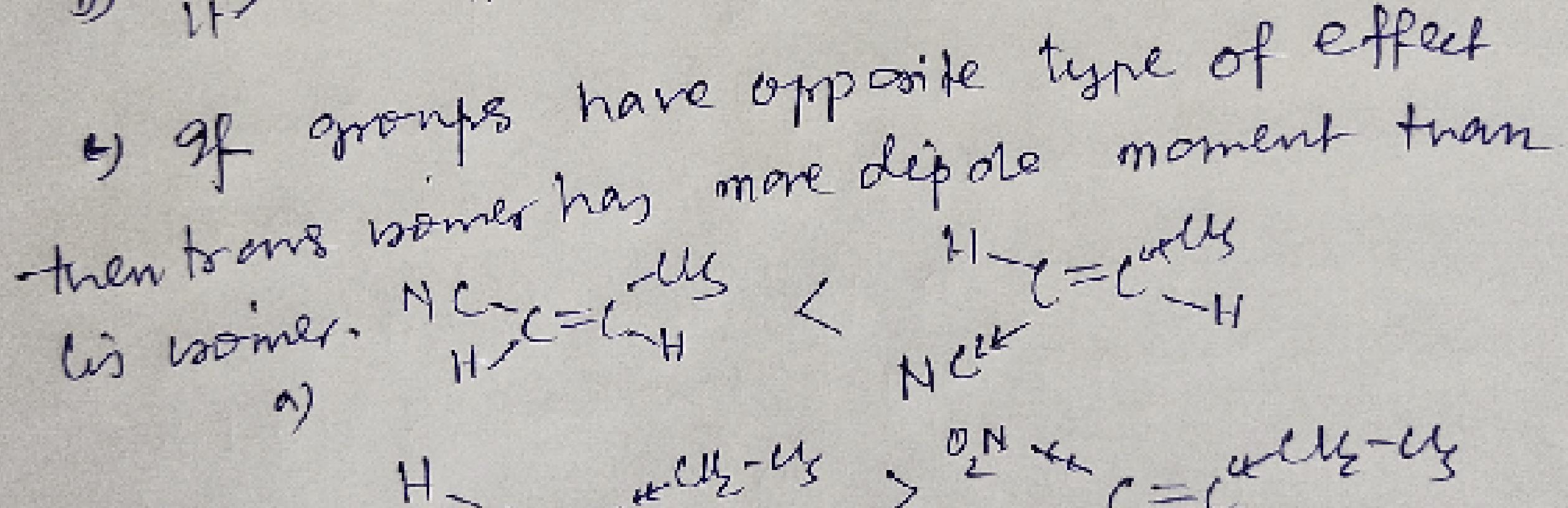
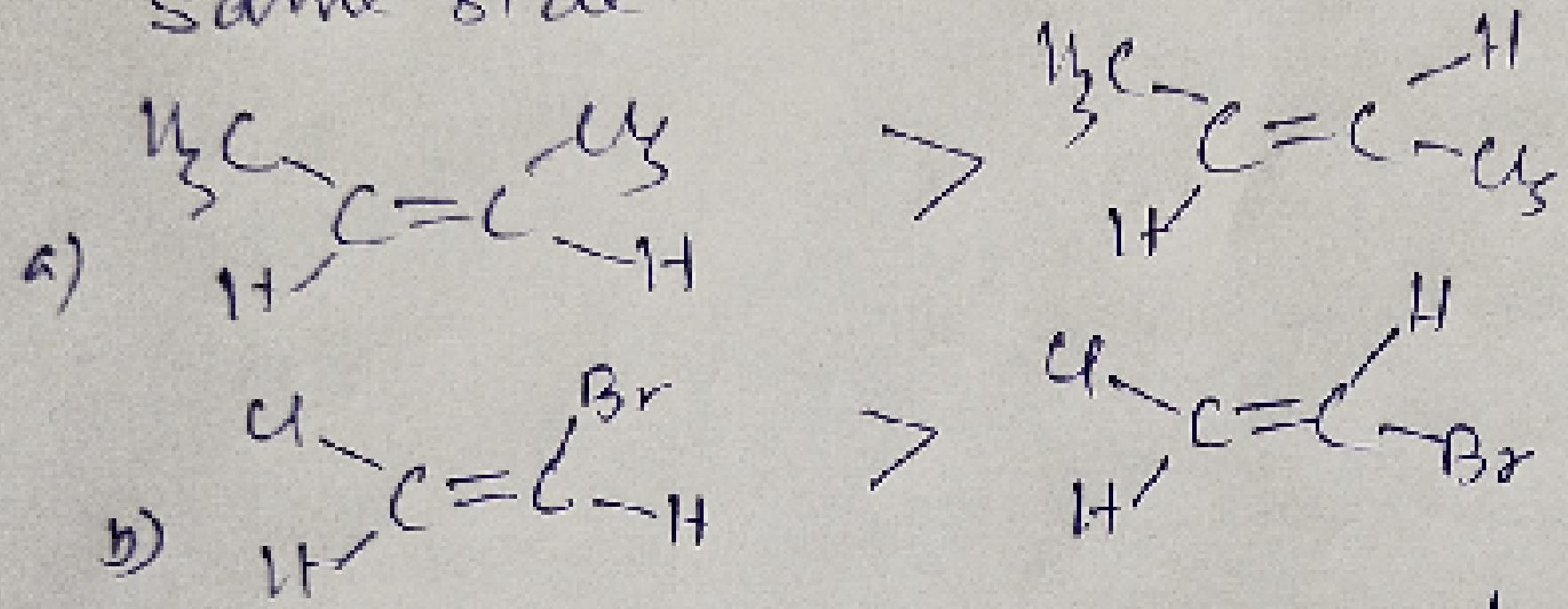
dipolemoment order: para > meta > ortho.



12

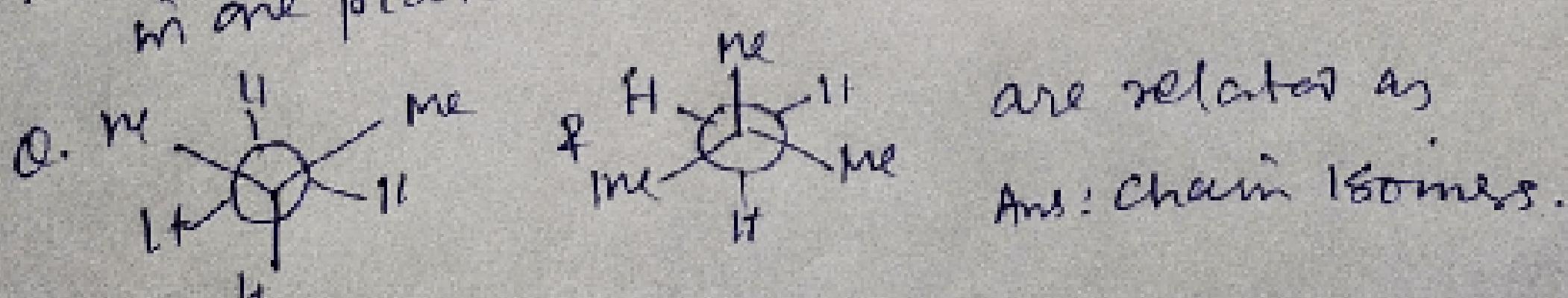


⇒ cis isomer has more dipole moment than trans isomer. If same groups or groups having same type of effect are in the same side.



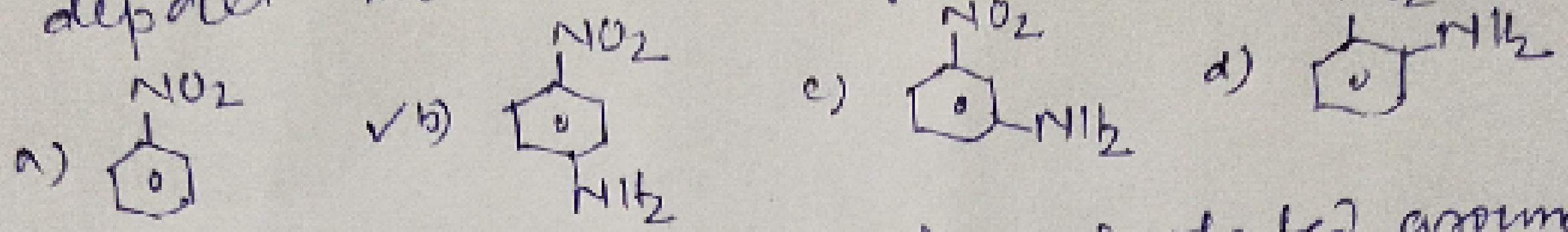
Q. Find out maximum no. of atoms present in same plane for Eclipsed structure of ethane. How many such planes are present.

Ans: There are 4 maximum atoms present in one plane & 6 such planes are present.

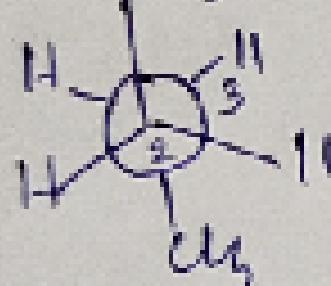


Q. Number of possible conformations of butane is 13
 a) 2. b) 4. c) 6. d) Infinite.

Q. Which of the following compound has maximum dipole moment among following?

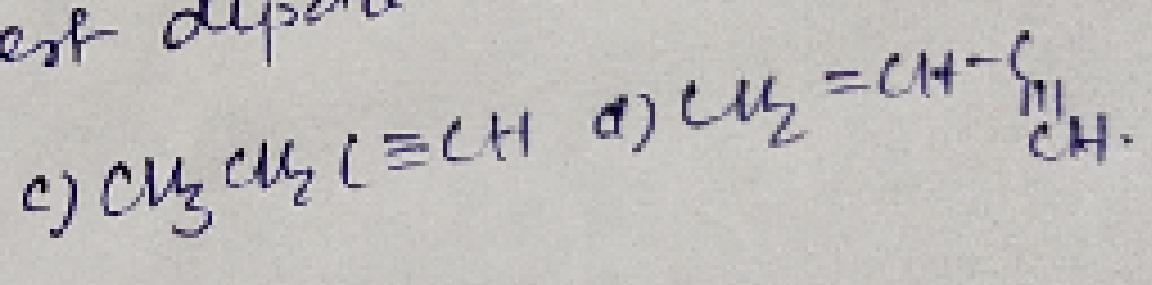
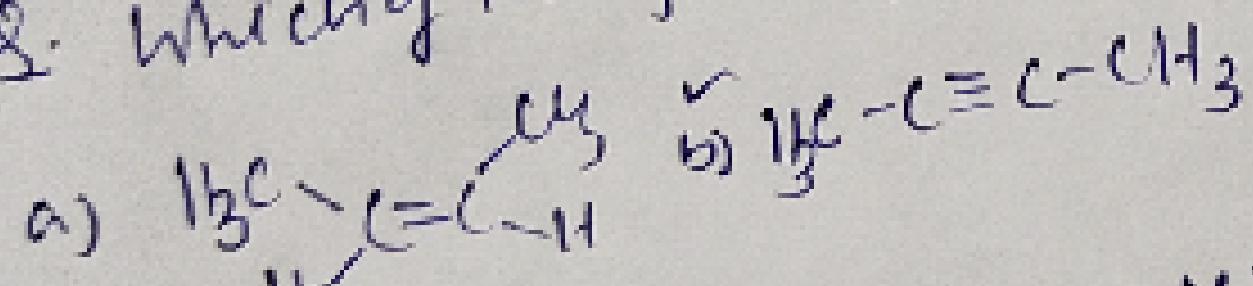


Q. In the given conformation, if C₂ is rotated around C₂-C₃ bond anticlockwise by an angle of 120°, then the conformation obtained is



- a) fully eclipsed conformation
- b) Partially eclipsed conformation
- c) Gauche conformation
- d) Staggered conformation.

Q. Which of the following has lowest dipole moment.



Q. $M_{obs} = \sum \mu_i x_i$ where μ_i = dipole moment of stable conformer of the molecule & x_i = mole fraction of the stable conformer.

Given $M_{obs} = 1.0$ Debye & $x(\text{anti}) = 0.82$ mole fraction.

Calculate the value of M_{gauche} .

$$M_{obs} = 1 \text{ Debye} = M_{\text{gauche}} \times 0.18 + M_{\text{anti}} \times 0.82$$

$$= M_{\text{gauche}} \times 0.18 + 0.$$

$$M_{\text{gauche}} = \frac{1}{0.18} = 5.55 \text{ Debye.}$$