

I MSc., CHEMISTRY
ORGANIC CHEMISTRY – I
SEMESTER – I
CODE: DCHII

UNIT – 2
CONFORMATIONAL ANALYSIS

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The catalyst -

unchanged. UNIT-II - CONFORMATIONAL ANALYSIS:-

CONFORMATIONS OF 1,2-disubstituted cyclohexanes:-

cis + trans 1,2-dimethylcyclohexane (Geometrical isomerism in 1,2)

(i) If one of the substituents of 1,2-disubstituted cyclohexanes is present in equatorial position and the other in axial position, the two substituents will be cis to each other. Such conformations are referred to as ae/ea.

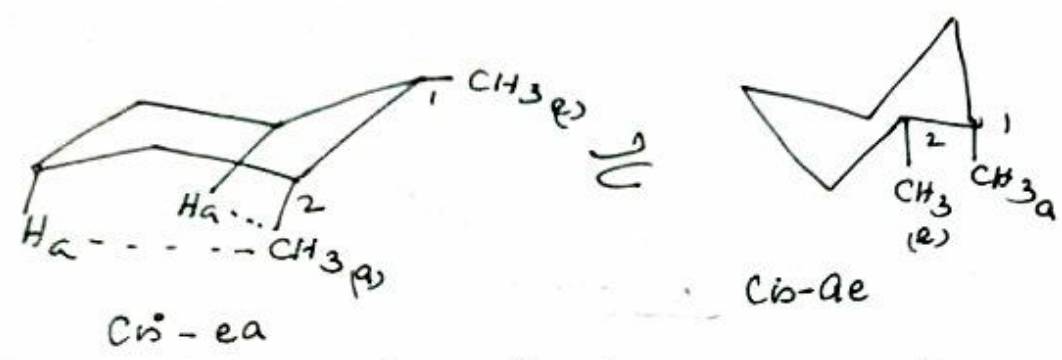
(ii) If both the substituents are in axial position or in equatorial position, the conformation is trans.

(iii) In cis, regarding their stabilities, both are equally stable since both of them

possess one methyl group in axial position.
 (iv) Stability can be explained on the basis of two factors

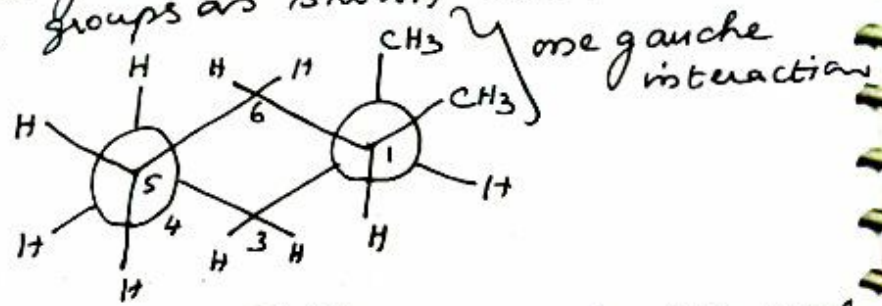
- (a) 1,3-diaxial interaction
- (b) Gauche interaction.

(v) In cis-1,2-dimethylcyclohexane, there is one axial group which causes two 1,3-diaxial methyl-hydrogen interactions as shown in Fig



(two diaxial interactions)
 Half of the molecules will exist in ea conformation and another half in ae)

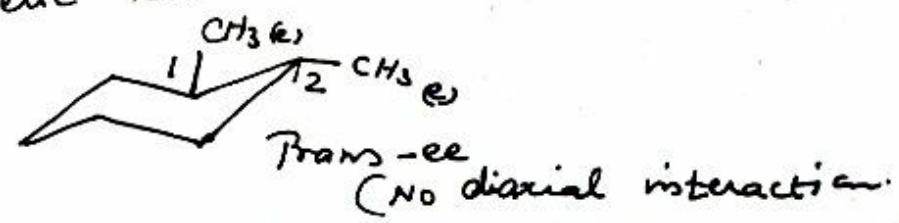
(vi) There is one gauche interaction between two methyl groups as shown below



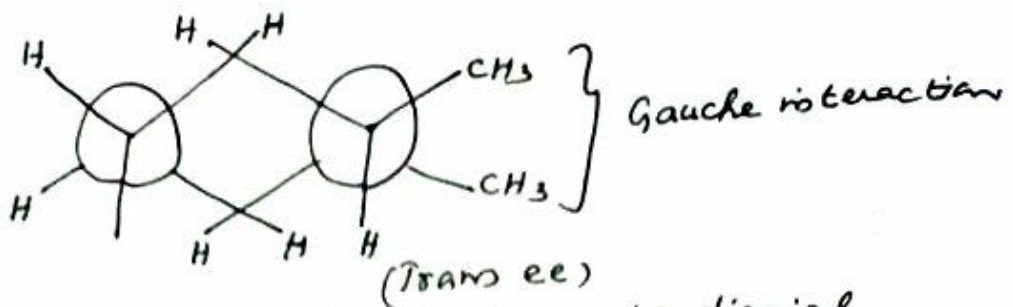
(vii) Thus on the basis of cis-ea 1,3-diaxial interaction / gauche interaction a total of (0.9×3) 2.7 kcal/mole of steric strain is present in cis-1,2-dimethylcyclohexane.

(viii) In diequatorial trans-1,2-dimethylcyclohexane there is no diaxial-1,3-interaction due to the absence of axial methyl group.

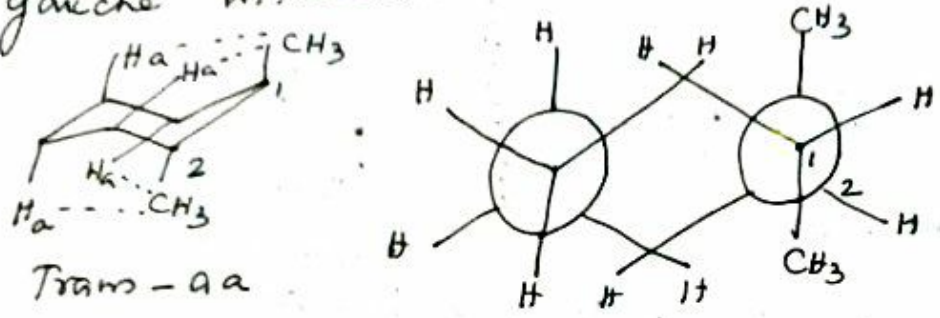
(ix) But there is one gauche interaction between the methyl groups which confers 0.9 kcal/mole of steric strain



(x)



(xi) Trans-aa form has four 1,3-diaxial interactions since both methyl groups are in axial conformation. Trans-aa form has no gauche interaction as shown below.

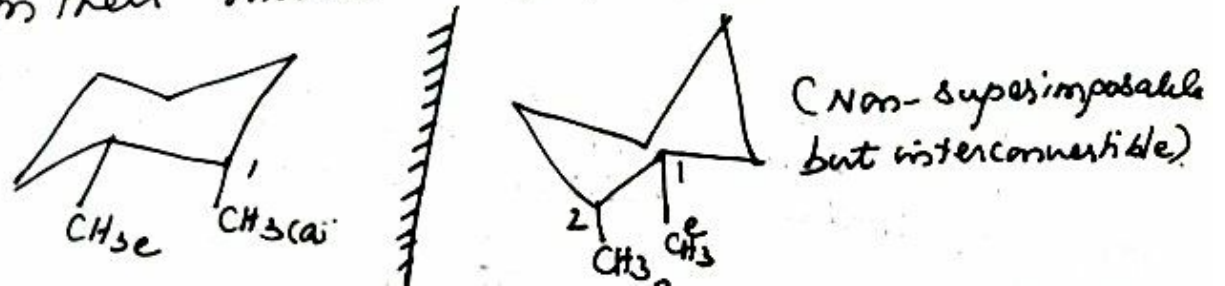


(xii) So ~~the~~ Trans-aa has (4×0.9) 3.6 kcal/mole of instability.

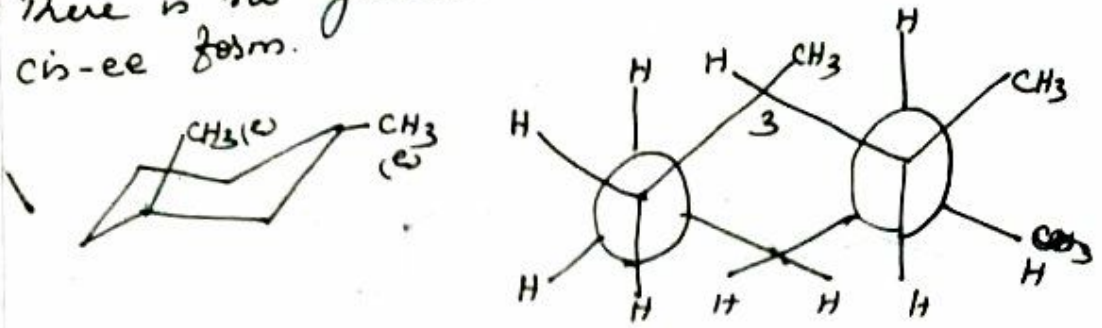
Conformers	Energy for interaction
(i) Trans (ee)	(i) 0.9 kcal/mole
(ii) cis ae/ea	(ii) 2.7 kcal/mole
(iii) Trans (aa)	(iii) 3.6 kcal/mole

order of stability is
 So $\text{Trans (ee)} > \text{cis ae/ea} > \text{trans aa}$
OPTICAL ISOMERISM IN 1,2-dimethylcyclohexane.

(i) ^{cis-}1,2-dimethylcyclohexane exists as ae/ea. They are energetically equivalent. Their chair conformations are not superimposable on their mirror images, as shown.

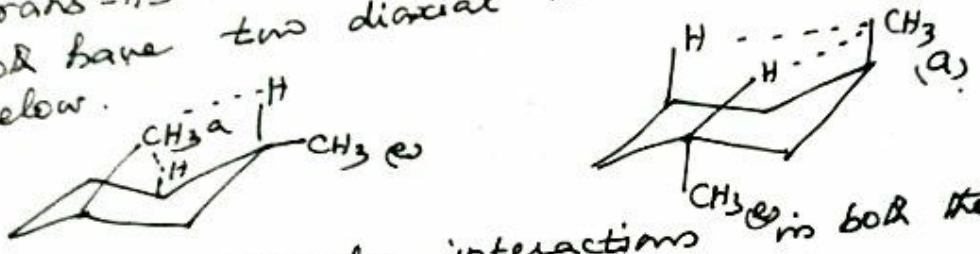


(V) There is no gauche interaction in cis-ee form.



(VI) So the cis-aa form is destabilised by $(2 \times 0.9 \text{ kcal/mole})$ or 1.8 kcal/mole of energy.

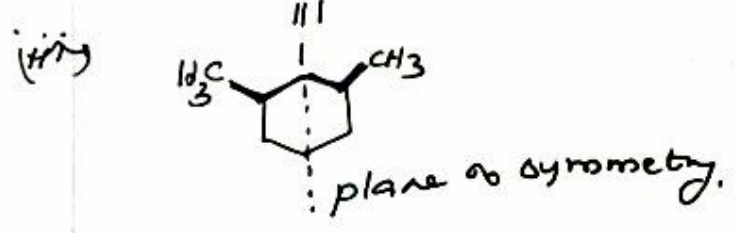
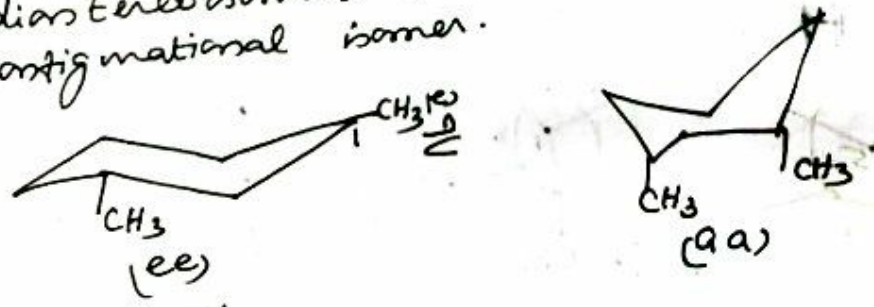
(VII) Trans-1,3-dimethylcyclohexane exists as ea/ae. Both have two diaxial interactions as shown below.



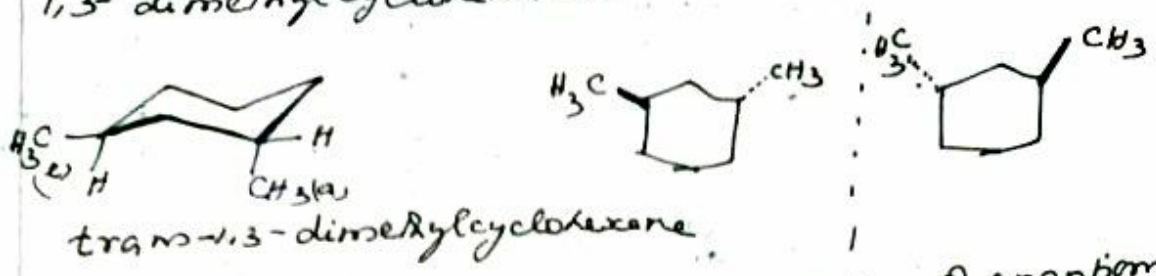
(VIII) There is no gauche interactions in both the cases. Order of stability is $\text{cis-1,3-(aa)} > \text{trans ae/ea} > \text{cis ee}$.

OPTICAL ISOMERISM:-

- (i) cis-1,3-dimethylcyclohexane exists as two energetically non-equivalent chair conformations which are achiral due to the presence of a σ -plane and so they constitute meso form.
- (ii) cis form has only conformational diastereoisomers and does not have configurational isomer.

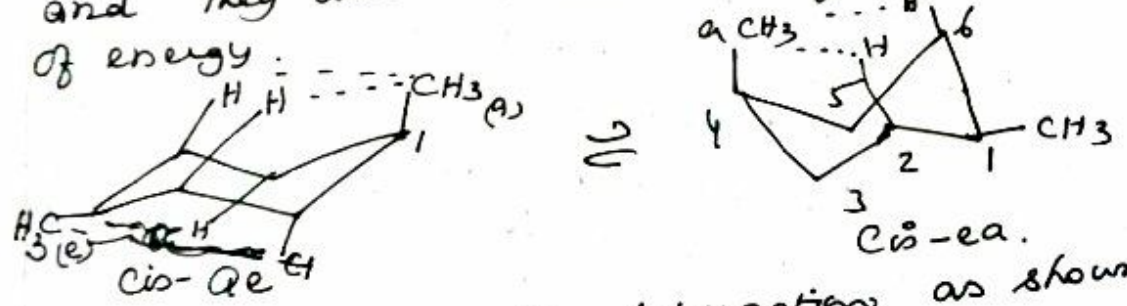


(iii) However no symmetry plane / centre of symmetry can be detected in the trans isomer. Thus there are two enantiomeric 1,3-dimethylcyclohexane.

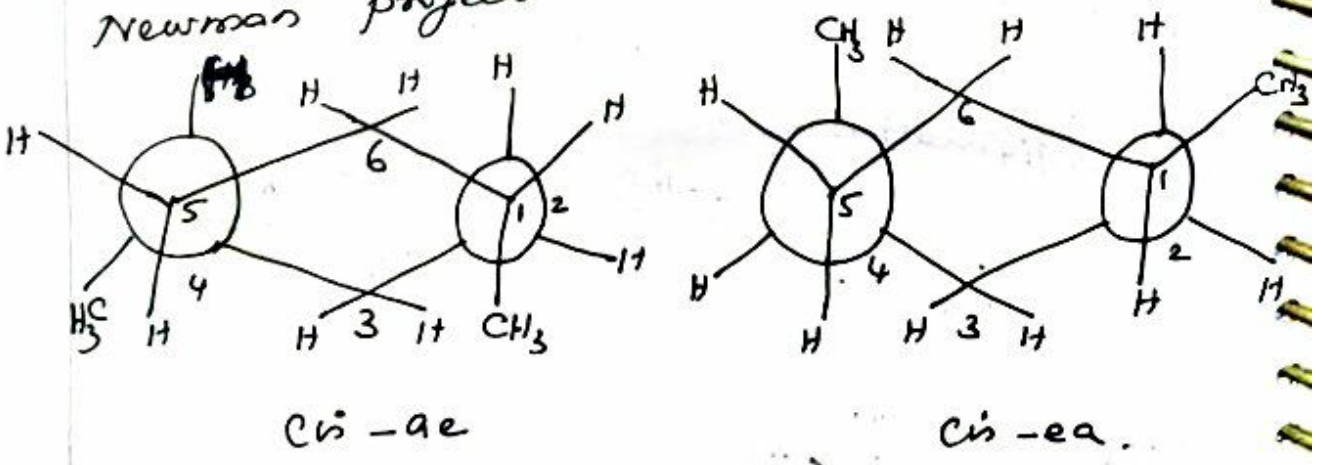


(iv) trans ae and trans ea are mirror images of each other and they are known as conformational enantiomers.
1,4-disubstituted cyclohexane:- Geometrical isomerism, cis form

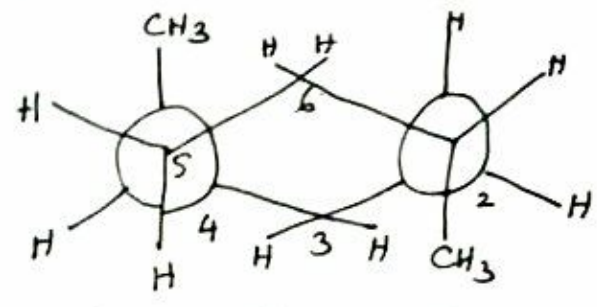
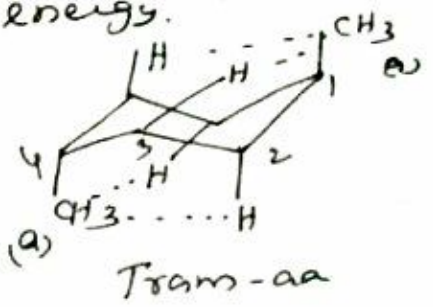
(i) In 1,4-disubstituted cyclohexane, cis exists as ae and ea.
 (ii) Both forms have two 1,3-diaxial interactions and they are destabilised by $(0.9 \times 2) = 1.8 \text{ kcal/mole}$ of energy.



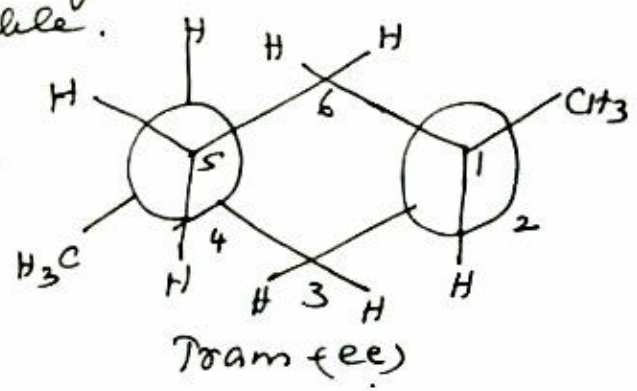
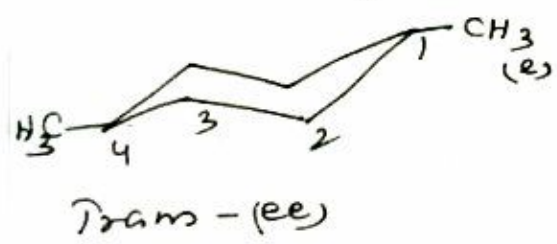
(iii) There is no gauche interaction as shown in Newman projection.



(iv) Trans-1,4-dimethylcyclohexanes exists as aa/ee form. Trans-aa form has four 1,3-diaxial interaction and there is no gauche interaction as shown below. So it is destabilised by $(4 \times 0.9) = 3.6$ kcal/mole of energy.

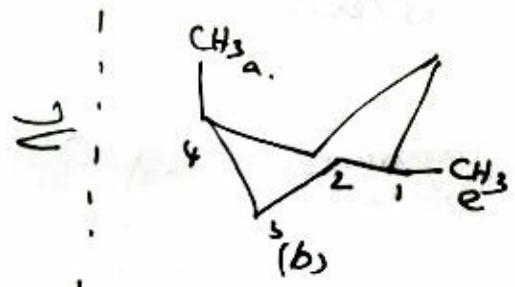
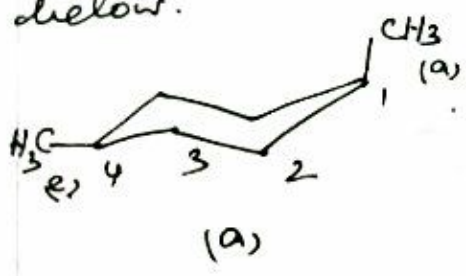


(v) Trans-ee form has no 1,3-diaxial interaction and no gauche interaction. So it is highly stable.



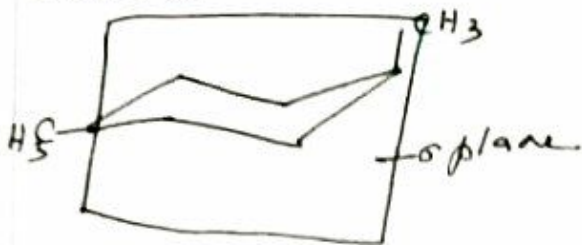
OPTICAL ISOMERISM:-

(i) Cis-isomer is achiral and exists as two conformational enantiomers. Cis ee and cis ea are mirror images of each other as shown below.

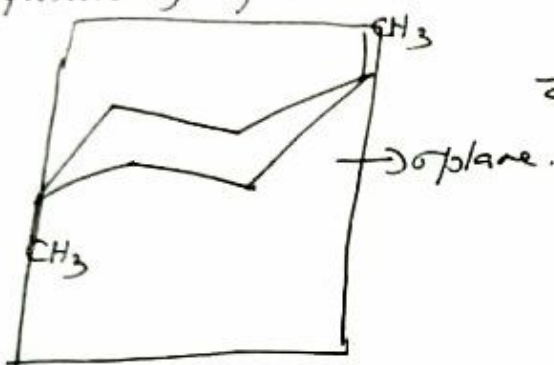


(ii) a & b are identical, energetically equivalent conformations. It has a vertical σ -plane passes through

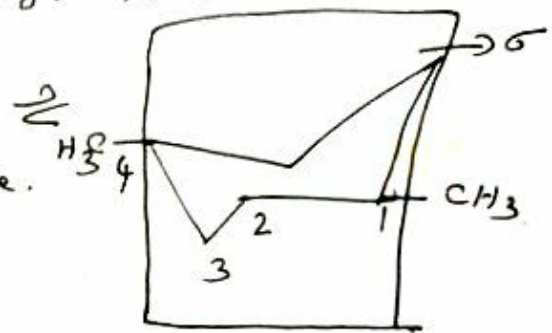
1,4-positions and the conformation is achiral.



(ii) Trans-1,4-dimethylcyclohexane exists either in aa or in ee. Both are energetically non-equivalent conformations. Both are achiral as a plane of symmetry passes through 1,4-positions.

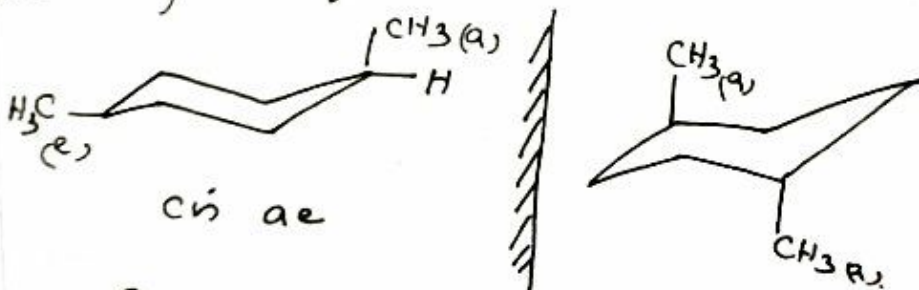


Trans aa



Trans-ee

iv) cis and trans 1,4-dimethylcyclohexane exists as a pair of diastereoisomers



Stereoisomers but not mirror images.