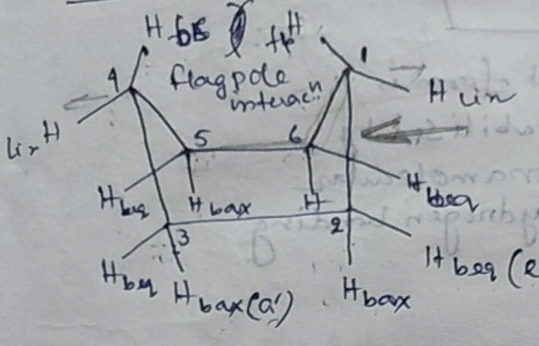
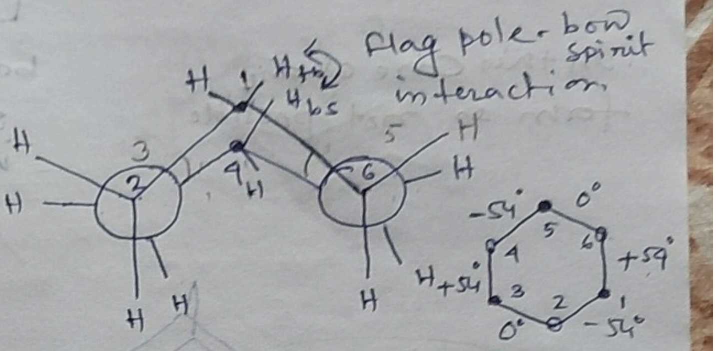
Mitali Dawan/B.Sc Chem(H) / SEM-V/C-12

Flexible conformers of cyclohexane:

Boat Conformation

Twist boat Conformation





Energy: (4 gb interaction + 2 eclipsed butane unit
(Enthalpy term)
(4 × 3.3) + (2 × 18.0) interaction)
= 49.2 kJ/mol

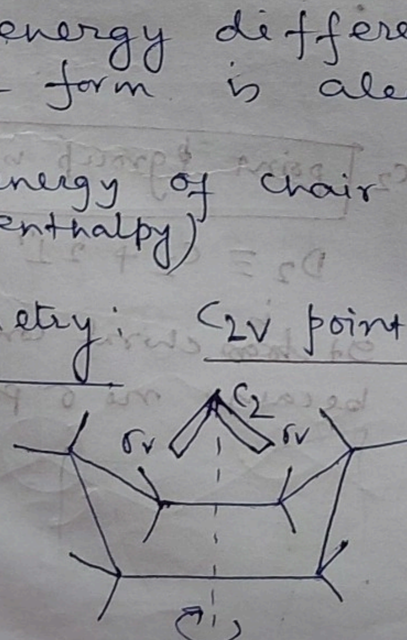
$C_2 - C_1 - C_6 - C_5$
$C_2 - C_3 - C_4 - C_5$
$C_3 - C_4 - C_5 - C_6$
$C_3 - C_2 - C_1 - C_6$

$C_1 - C_2 - C_3 - C_4$
$C_1 - C_6 - C_5 - C_4$

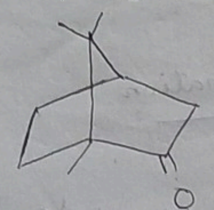
Flagpole interaction — ~~There is~~ The two 1r hydrogens at C-1 and C-4 in only 183 pm away giving rise to a non-bonded interaction, known as flagpole - bow spirit interaction.

- Due to these three types of interaction the boat form is less stable than chair form. The energy difference between boat & chair form is about ~~29.~~ (29.4 - 45.4) kJ/mol
- The energy of chair form (enthalpy) 19.8 kJ/mol.

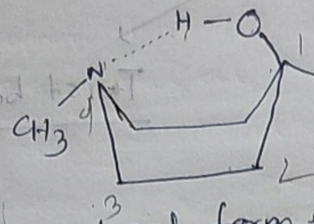
Symmetry: C_{2v} point gr. ($C_2 + 2\sigma_v$)



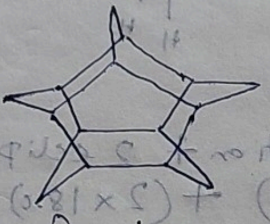
⊛ under certain condition boat can be stabilised in preference to chair.



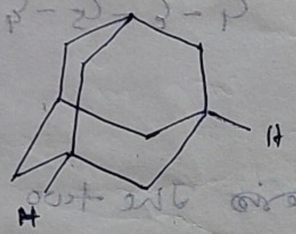
In this case chair form is not possible



boat form is stabilised by intramolecular hydrogen bonding



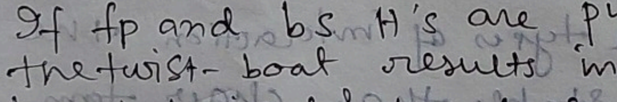
fixation of boat form.
pentaasterane



Adamantane
fixation of chair form

Twist-boat conformations

If fp and bs H's are pulled a little apart, the twist-boat results in which the fp-bs interaction is minimised & the conformation become more stable.



Twist cyclohexane

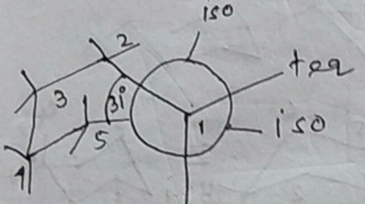
$\boxed{\text{point group is } D_2}$

$D_2 \equiv C_2 + 2\perp^r C_2$

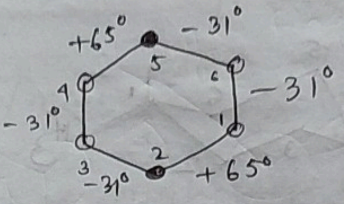
It ~~has~~ is chiral conformation because no σ plane.

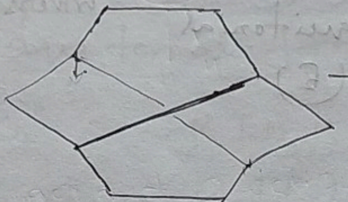
iso (isoclinical)
tax (twist axial)
teq (twist equitorial)

Twist boat $\rightleftharpoons$ boat interconversion take place without bond angle changes. The only changes are in torsional angles and these interconversions are called pseudorotation.



Newman projection of twist boat form





→ Fixation of twistboat form in twistane.

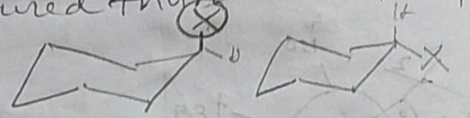
~~This twist fo~~
→ This twist-boat form is stabilised in preference to chair form due to electronic effect.

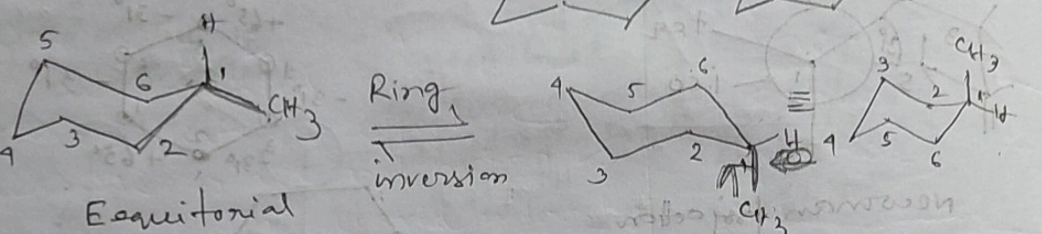
Points to be noted

- ⊛ The twist conformation of cyclohexane is sometimes called skew-boat.
- ⊛ It is more stable than boat by 3.7 kJ/mol, probably due to the decrease in torsional strain.
- ⊛ bat form and twist-boat forms are flexible form.
- ⊛ These two forms are high-energy conformation but their entropy is high due to more degree of freedom than the chair form.
- ⊛ The population of flexible form is approximatly 1 in 1000.

⊛ Conformation of monosubstituted cyclohexane:

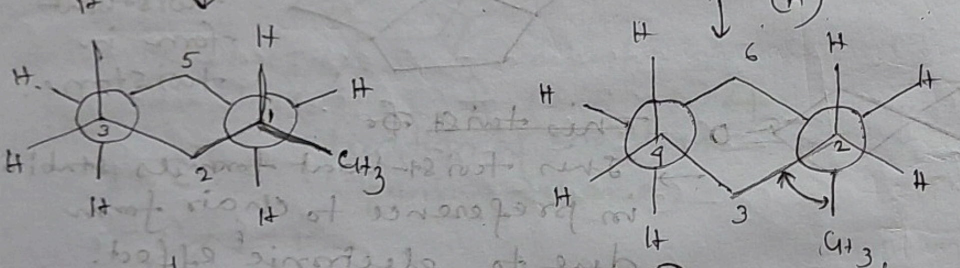
In case of chair conformation of monosubstituted cyclohexane, the equitorial conformation of substituent is more favoured than the axial form.





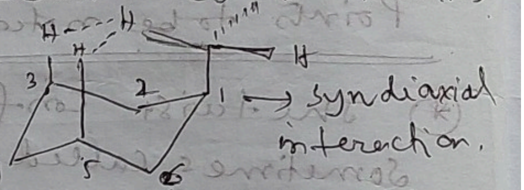
Equitorial (E)

Axial (A)



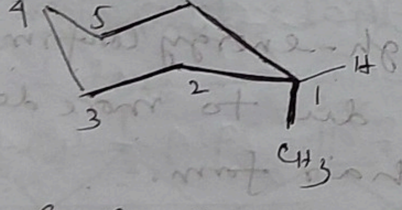
This form has six gb interaction similar to normal cyclohexane.

~~Boat~~ ⊛ But this form has two additional g-b H interaction.



→ syn diaxial interaction.

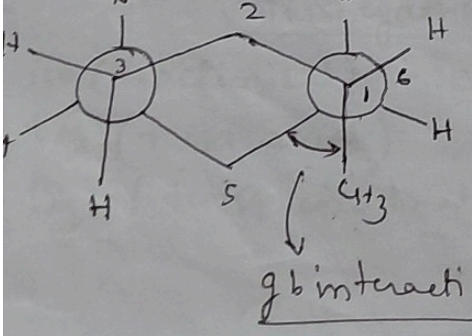
⊛ In ~~Aax~~ Axial form the additional gb interaction is shown by thick line in chair form



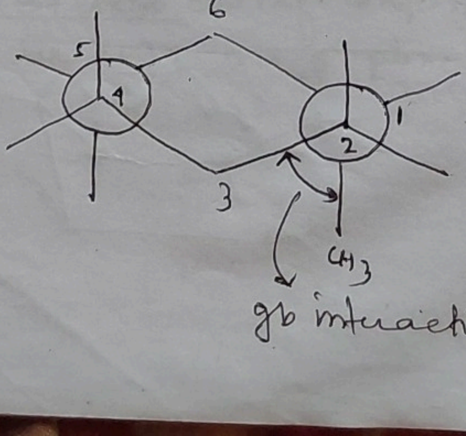
Due to this steric effect ~~of~~ between -CH$_3$ proton and protons of 3 & 5 position axial form is destabilised and equillibrium shifted towards equitorial form. This ~~co~~ is called syn-1,3 and syn 1,5 ~~diaxi~~ diaxial interaction.

$Me - C_1 - C_2 - C_3$

$Me - C_1 - C_6 - C_5$



and



∴ The difference of Enthalpy (ΔH) between the axial and equitorial is (2×3.3) kJ/mol = 6.6 kJ/mol.

If ΔG is equated to ΔH (ΔS = 0).

Then $\Delta G_{(E-A)} = -6.6$ kJ/mol.

or $\Delta G_{A-E} = 6.6$ kJ/mol.

$A \rightleftharpoons E$

$\Delta G = -6.6$ kJ/mol.

$K = \frac{[E]}{[A]}$

(*) Higher the value of −ΔG, higher is the population (or %) of equitorial form.

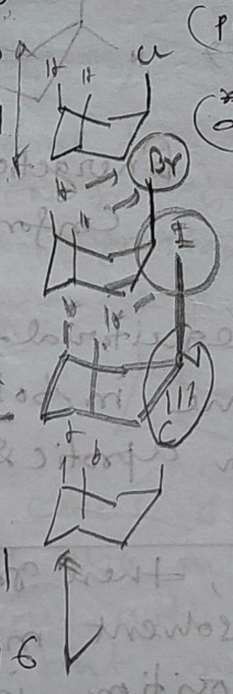
we know that $\Delta G^\circ = -RT\ln K$

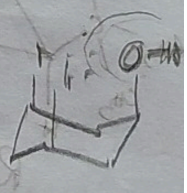
where $K = \frac{[E]}{[A]}$

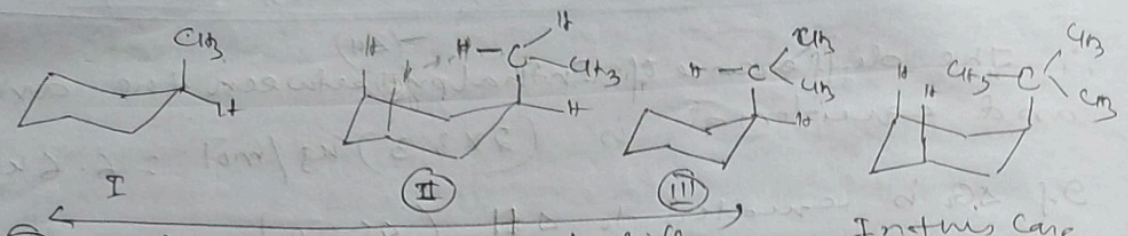
from this equation it is calculated that the population of equitorial conformer is over 90%. (actually 95% shown by NMR) at ambient temperature.

(*) Conformational free energy (−ΔG°) in kJ/mol for some common substituents.

Substituent	−ΔG°	Substituent	−ΔG°
F →	0.63	NH_2 (polar protic) →	6.70
Cl →	1.80	NH_2 (~~non polar~~ aprotic) →	5.03
Br →	1.59	NO_2 →	4.60
I →	1.80	CO_2H →	5.65
CN →	0.71	CO_2Me →	5.32
OH (inaprotic solvent) →	2.18	CH_3 →	7.50
OH (protic solvent) →	3.65	C_2H_5 →	8.10
OCH_3 →	2.51	$CH(CH_3)_2$ →	9.00
OC_2H_5 →	2.96	$C(CH_3)_3$ →	20.00
$OCOCH_3$ →	2.51	C_6H_5 →	12.60





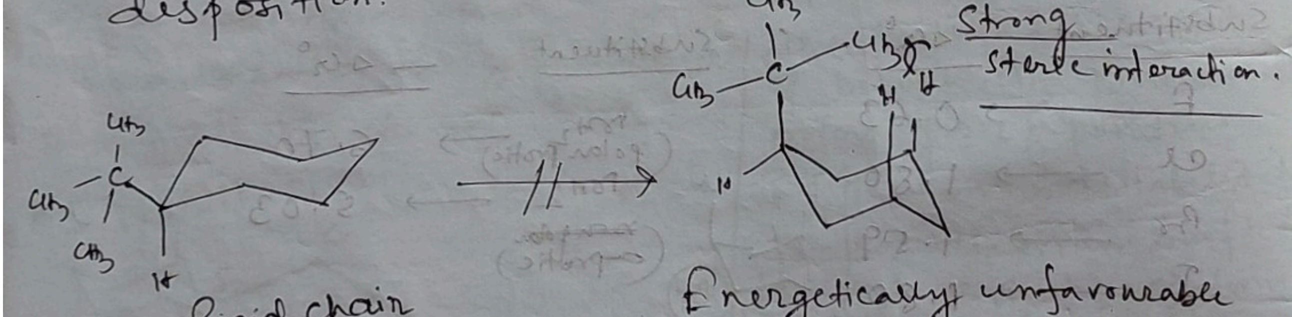


(*) ΔG° values are ~~xx~~ not differ abruptly because the first CH_3 gr in II & two me gr. in III are oriented in such a manner that the effective bulkness ~~is~~ are not increases abruptly. So syn-diaxial interaction is not increases effectively.

Actually ~~Because~~ here α-Hydrogen is turned inward, so syn-diaxial interaction is minimized.

In this case three me gr. is present so it has highest effective bulkness. & it has no αH atom that can turned inward to minimize the syndiaxial interaction. So $-\Delta G^\circ$ value is abruptly high.

(*) Actually the high conformation energy of t-butyl ensures that the group has an almost total preference for equitorial disposition.



Rigid chair

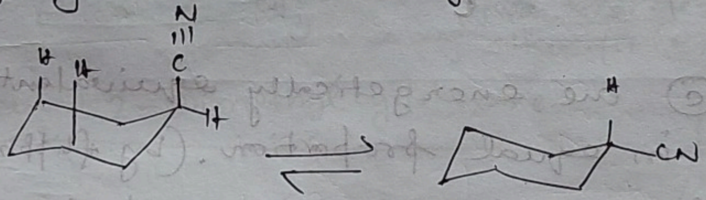
Energetically unfavourable Conformation.

(*) The ~~xx~~ population of equitorial form of cyclohexane containing NH_2, OH, NHMe in polar protic solvent is greater than that in aprotic solvent ($\Delta G^\circ_{protic} > \Delta G^\circ_{aprotic}$)

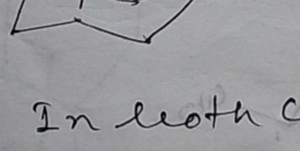
In polar protic solvent, these grs (NH_2, OH, NHMe) form H-bond with solvent molecule. So effective bulkness of these gr. in axial position increases (and ΔG° increases) & therefore population of equitorial conformation increases to avoid extra steric interaction in axial position.

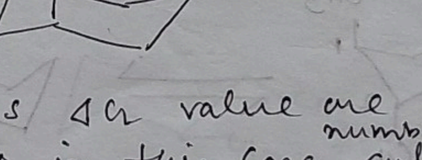
⊛ In halogen series f has least effective bulkness as expected. So Conformational free energy is least.
The conformational free energy of Cl, Br, I are almost equal, beause with increasing size of halogen C–X bond length also increases. So distance between synaxial hydrogen also increases. so ~~bulkness~~ conformational free energy nearabout same.

⊛ The population of ~~Aa~~ Axial & Equitorial is nearabout same in case of –HgBr gr. In this case the conformational free energy is zero. This is due to great length between ring carbon and Hg atom of HgBr and easy polarisability of Hg atom bearing partial +ve charge.



Conformational free energy is low because as CN gr. is linear, it exerts very small ~~diaxial~~ syn diaxial interaction.





In both cases ΔG value are nearabout same beause also in this case number substituent is ~~present~~ increases with the first atom connected to the ring but number of substituent does not increases ~~direct~~ with direct carbon of cyclohexane. And ~~to~~ in these compd. the substituents are oriented in such a way that effective bulkness remain more or less constant.

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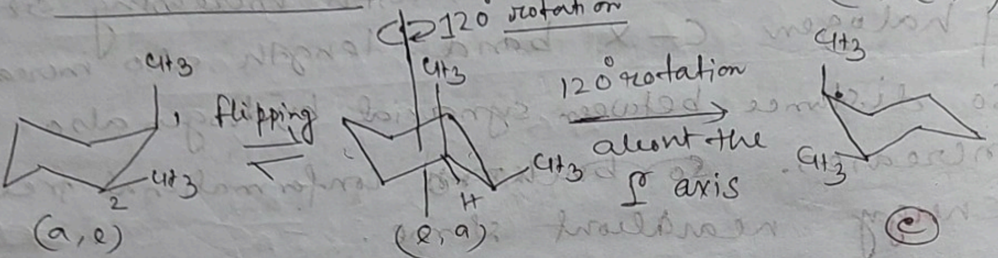
Conformation of Disubstituted Cyclohexane

① 1, 2 - Dimethyl cyclohexane :

cis-1,2-dimethylcyclohexane (a,e), (e,a)

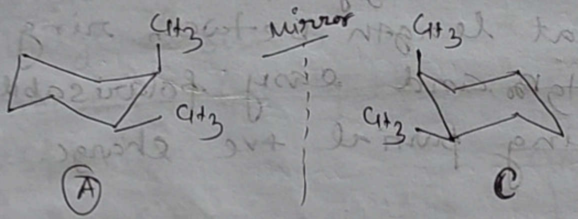
trans-1,2-dimethylcyclo~~h~~ hexane. (a,a) (e,e).



Ⓐ Ⓑ Ⓒ

B & C are identical

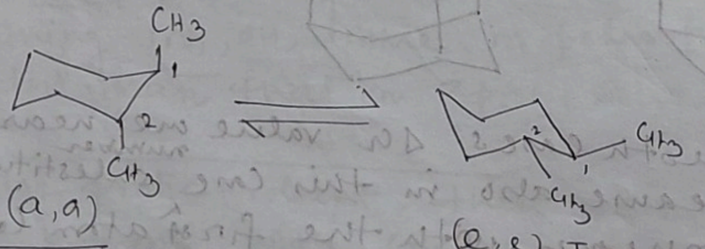
Now Ⓐ & Ⓒ are mirror image to each other but non superimposable.



So A & C are enantiomer.

Since Ⓐ & Ⓒ are energetically equivalent so they exist in equal proportion. (by flipping).

The cis isomer have only C_1 point group so ~~a~~ it is chiral. But due to presence of both ~~mirror~~ enantiomer in equal proportion they exist as non-resolvable d/l pair.

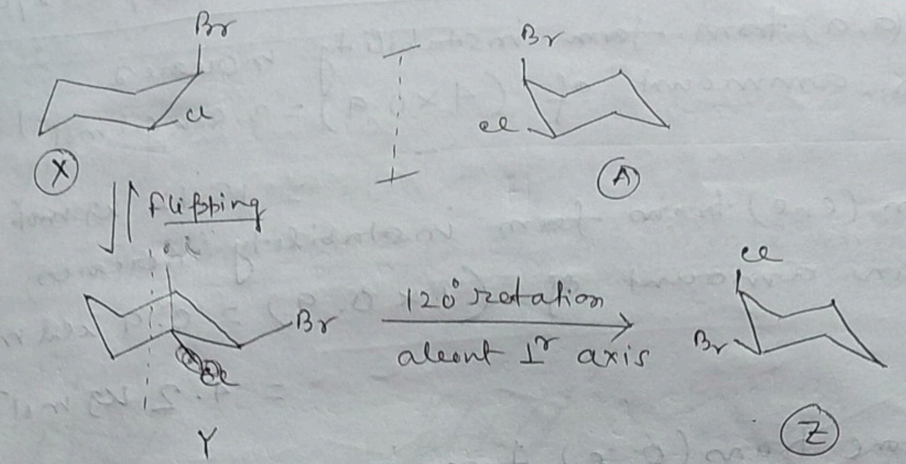


Trans (a,a)   (e,e) Trans.

~~They have diastereotopic~~

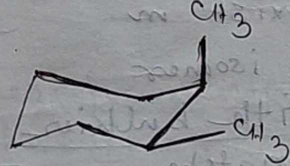
They are diastereoisomer.

Both (a,a) & (e,e) are chiral (having C_2) & can exist as resolvable (±) pair.



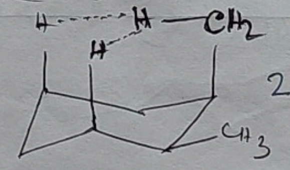
~~Here X & Z~~ Here Z & A are not identical. so X & Z have no mirror image relationship. i,e X & it's flipped str. Y are not enantiomer. so each X & Y are resolvable & the relation between X & Y are diastereomeric & energetically non-equivalent.

Stability of cis- & trans-isomer



→ 3 g.b interaction arises from two for one axial Me gr. (+ other for (e,a) dimethyl

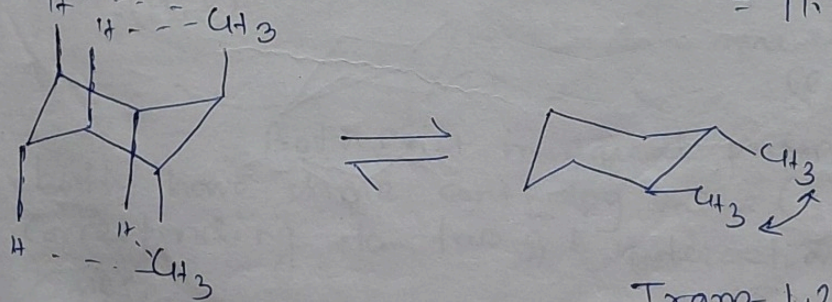
cis-1,2-Dimethylcyclohexane.



2(1,3-diaxial interaction)

Due to three g-b interaction, the instability of the system increases by an amount of (3 × 0.9) = 2.7 KCal mol^{-1}

= 11.2 KJ mol^{-1}.



Trans-1,2-dimethyl cyclohexane (a,a)

4 gb interaction + 4 1,3-diaxial interaction.

Trans-1,2-Dimethyl cyclohexane (e,e)

Only one g.b interaction. (between (e,e) Me gr).

So in (a, a) trans form instability increases by an ammount of $(4 \times 0.9) = 3.6$ kcal mol^{-1}

$= 15.12$ kg mol^{-1}.

And in (e, e) trans form instability increases by an amount of $(1 \times 0.9) = 0.9$ kcal mol^{-1}

$= 4.2$ kg mol^{-1}!

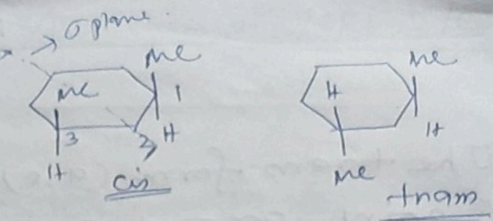
Therefore trans (e, e) form is more stable than tram (a, a) conformation by an amount of $(3.6 - 0.9)$ kcal mol^{-1}.

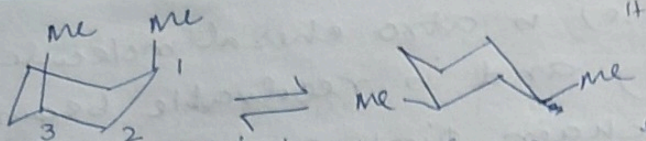
Actually the ratio of (a, a) : (e, e) is 1 : 99 at 25°C.

~~As~~ tram isomer almost exist in (e, e) form so tram isomer is more stable than cis-isomer.

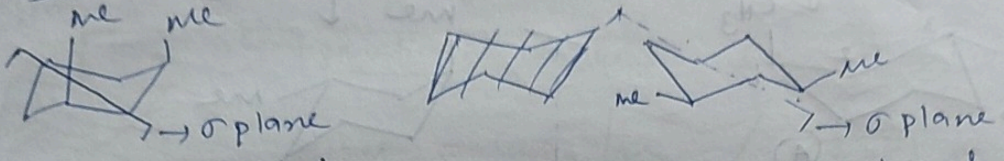
(*) When two substituents in the cyclohexane ring are different, both the cis and trans isomer are resolvable. The tram isomer exist in diequitorial conformation & the cis isomer in equitorial- axial conformation with bulkier group at the equitorial predominately.

1, 3 di~~[illegible]~~ methyl cyclohexane :



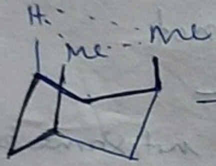


(a, a) 2 gb interaction (e, e) extra no gb interaction.
cis cis



so achiral achiral.

so cis 1, 3-dimethyl cyclohexane is meso due to this σ plane.

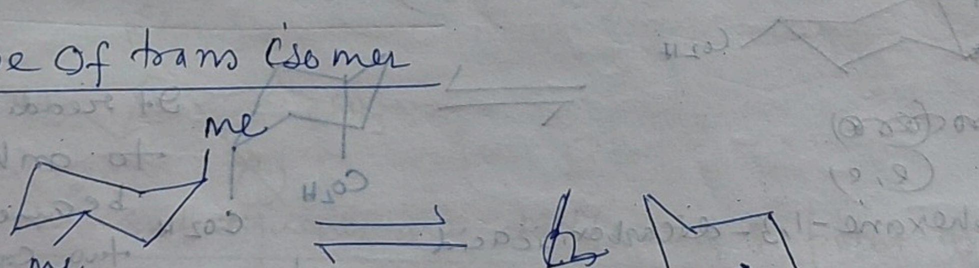


→ 2 gb interaction + one CH_3/CH_3 1,3-diaxial interaction.
7.5 KJ mol^{-1} 15.5 KJ mol^{-1}

∴ Total energy (enthalpy) = (7.5 + 15.5) KJ mol^{-1}
= 23 KJ mol^{-1}

⊛ Therefore enthalpy of diaxial form is 23 KJ mol^{-1} higher than that of diequitorial form making the former almost non-existent. (1 in 10,000 at 25°C).

In Case Of trans isomer

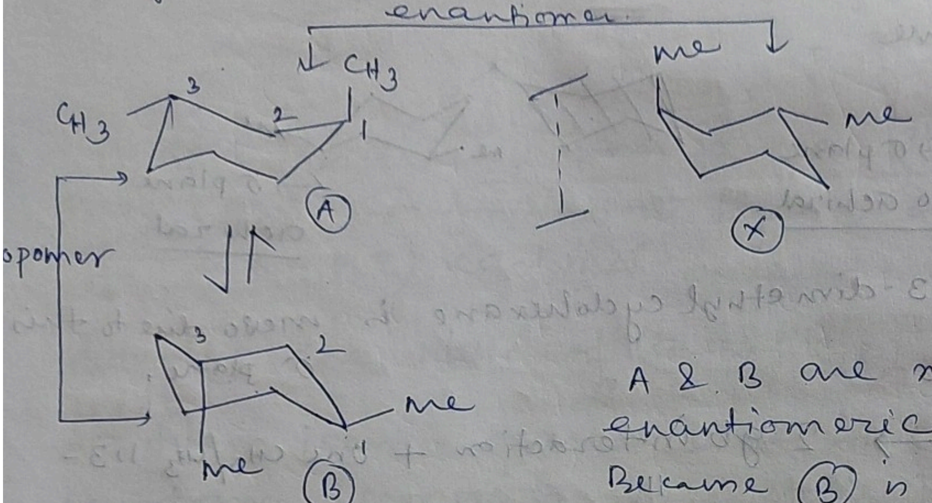


(a, e) (e, a)

Both exist in equal proportion because both have same enthalpy value (7.5 KJ mol^{-1}) Corresponding to two g.b interaction for both cases.

Thus 1, 3 cis isomer (e, e) is more stable than 1, 3 trans isomer.

The trans form (a,e) is also chiral molecule (point group C_1) and is resolvable became flipping of one chair into another does not produce the mirror image enantiomer.

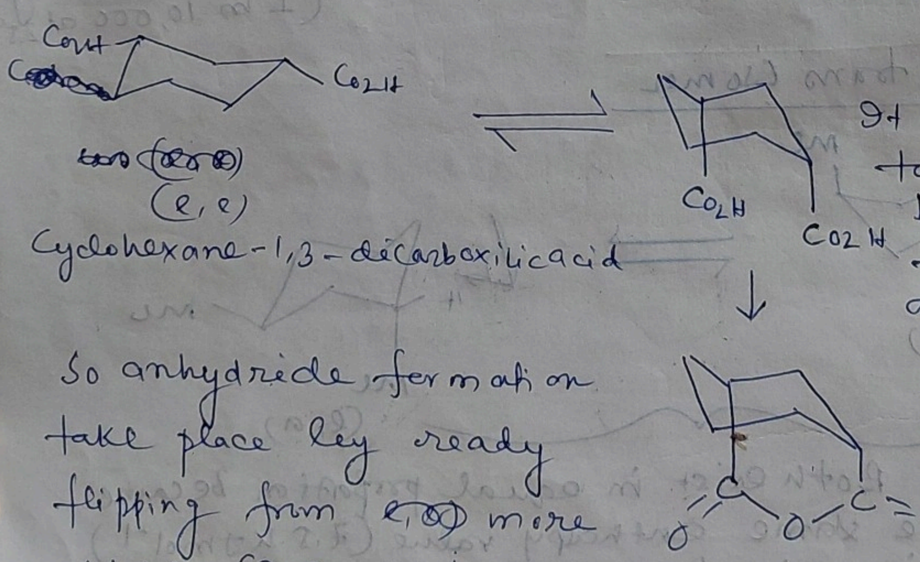


Flipped structure.

A & B are not enantiomeric Became (B) is not same to X.

Actually (A) & (B) are same (topomer) & they are superimposable.

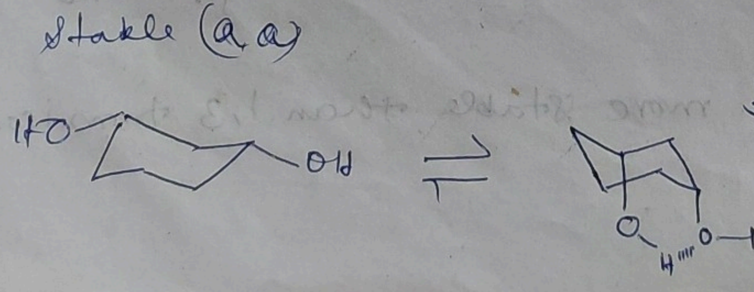
Certain diaxial form may became stabilized through intramolecular bond formation.



(e, e)
Cyclohexane-1,3-dicarboxilicacid

It readily convert to anhydride became the two CO_2H gr. are closer to react

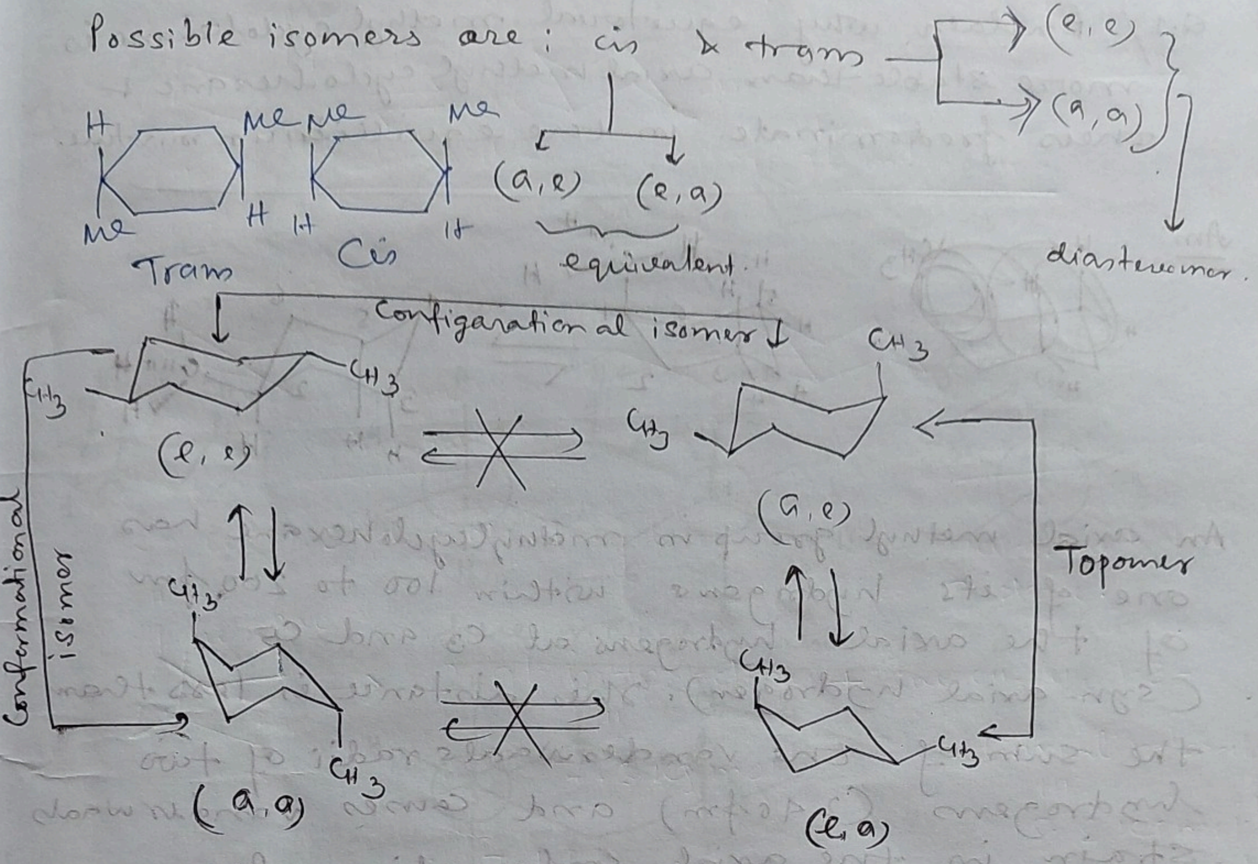
So anhydride formation take place by ready flipping from e,e more stable (e,e) to less stable (a,a)



Here 1,3 diaxial form is stabilized through intramolecular H-bonding.

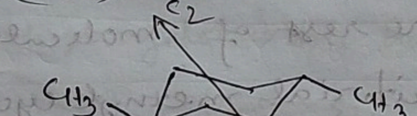
1,4 dimethylcyclohexane :

Possible isomers are : cis & trans

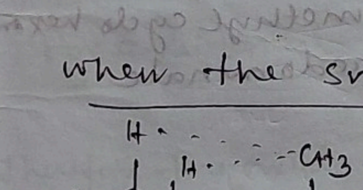


1,4-disubstituted cyclohexane is achiral due to having a vertical plane of symmetry passing through C_1 & C_4.

For identical substituents, point groups for (a, a) & (e, e) are C_{2h}. ($C_2 + \sigma_h$).

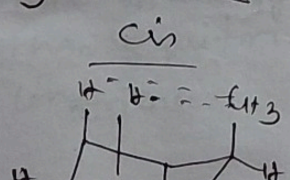


When the substituents are different, point group C_s (only σ plane).



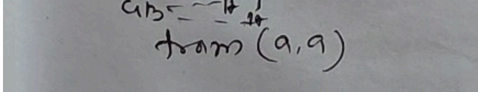
cis

→ 2 gb interaction (2×0.9 kCal = 1.8 kcal/mol or 7.5 kJ mol^{-1}).



trans (a, a)

→ 4 gb interaction (4×0.9 = 3.6 kcal/mol = 15.1 kJ/mol).



tran (e, e)

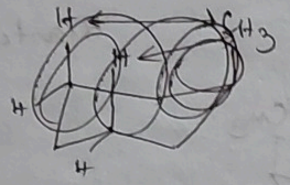
→ no additional gb interaction.

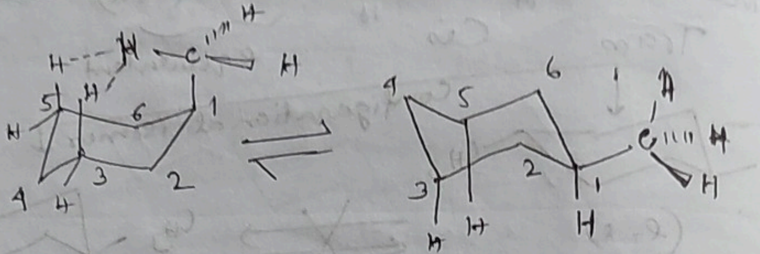
∴ (a, a) isomer is less stable than (e, e) isomer.

Question / Answer.

Q.1/ Explain why equitorial methyl cyclohexane is more stable than axial methyl cyclohexane & thus fredominate in the equillibrium mixture.

Ans:

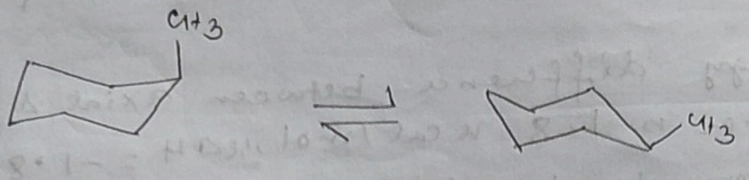




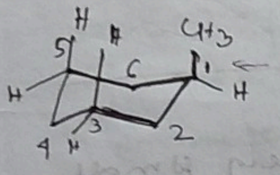
An axial methyl group in methylcyclohexane has one of its hydrogens within 100 to 200 pm of the axial hydrogens at C_3 and C_5 (syn-axial hydrogen). This distance is less than the sum of the vanderwaals radii of two hydrogens (240 pm) and causes vanderwaals strain in the axial conformation. Because the interacting substituents are on 1,3 positions relative to each other, these unfaromalele steric interaction are called 1,3-diaxial interactions or syn-axial interaction. when me-gr. in equitorial ~~form~~ it experiences no significant crowding as it is anti to C_3 & C_5 carbons. Therefore, the substituents extends into space away from the rest of molecule. Because of this, equitorial methyl cyclohexane is more stable than axial methyl cyclohexane and as a consequence it predominate in the equillibrium mixture.

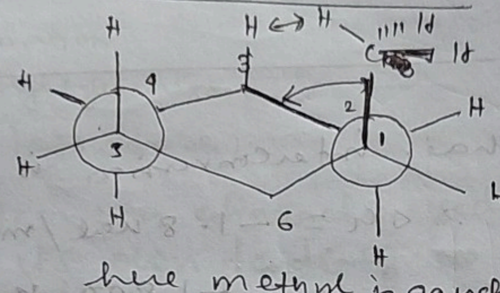
Q what is the energy difference between the two conformation of methyl cyclohexane?

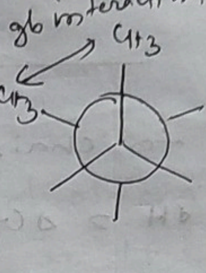
Ans:



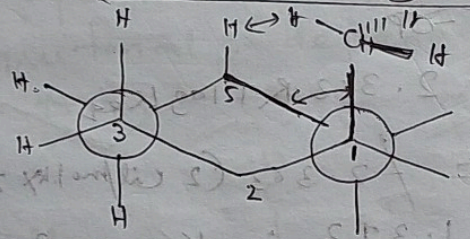
Two conformation







here methyl is gauche to C-3.

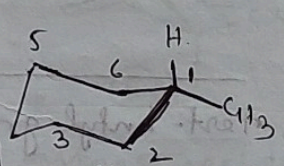


methyl is gauche to C-5.

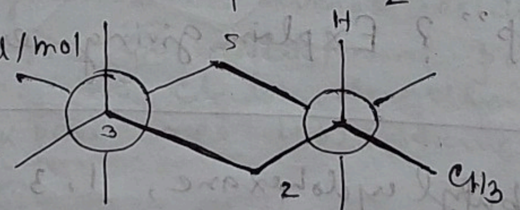
Thus for each 1,3 - diaxial methyl-hydrogen interaction there is a butane-gauche interaction between the methyl gr. and a carbon atom of the ring. For each gb interaction, the increase of energy of the system is 0.9 kCal/mol. ∴ Since axial conformation of methyl cyclohexane ~~have~~ has two gb interaction,

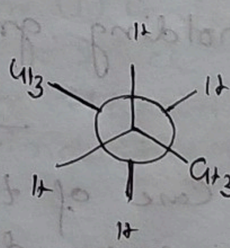
So energy = (0.9×2) = 1.8 kcal/mol.

For equitorial methyl

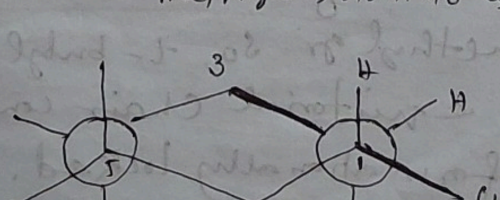


Therefore the axial conformer is 1.8 kCal/mol more in energy than equitorial conformer.





methyl is anti to C5



∴ no gb additional gb interaction.

for equitorial conformation

methyl is H anti to C3

③ Calculate the equillibrium constant (Keq) at 25°c for the equillibrium: axial methyl cyclohexane ⇌ equitorial methyl cyclohexane

The energy difference between axial & equitorial conformer is 1.8 kcal/mol (i.e $\Delta H = -1.8$ kcal/mol) and from that calculate the percentage of composition of the mixture.

ΔS for chair-chair interconversion is very small

$\therefore \Delta H \approx \Delta G \quad \therefore \Delta G = -1.8$ kcal/mol

$= -1800$ kcal/mol

Since

$$\Delta G = -2.303\, RT \log K_{eq}$$

$$\therefore \cancel{-}1800 = \cancel{-}2.303\,(2\ \text{cal/mol.K} \times 298\ \text{K}) \log K_{eq}$$

$\therefore \log K_{eq} = 1.313 \quad \therefore K_{eq} = 20.6$

now, $K_{eq} = \frac{[E]}{[A]} = \frac{20.6}{1}$

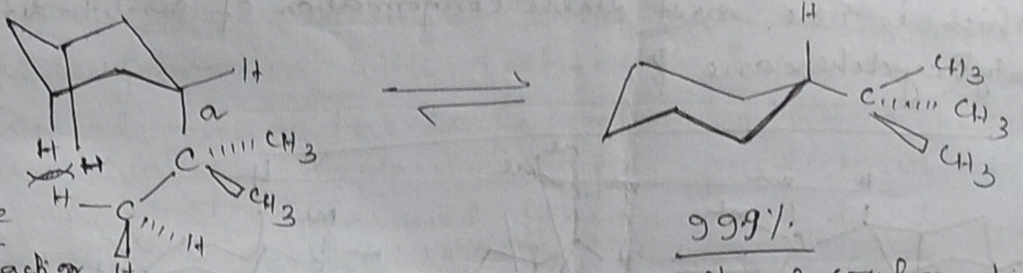
$$\therefore \%\ \text{of}\ [E] = \frac{[E]}{[E]+[A]} \times 100$$

$$= \frac{20.6}{20.6+1} \times 100 = 95\%$$

$\therefore \%$ of $[A] = (100 - 95) = 5$.

Q ④ Explain why tert-butyl group characterized as a "holding group"? Explain giving example.

Ans in Case of t-butyl cyclohexane, 1,3 diaxial interaction are more destabilizing, because it is much larger than methyl gr. So, t-butyl cyclohexane almost exist in equitorial chair conformation. i,e it is conformationally locked.



Severe steric interaction (1,3 diaxial interaction)

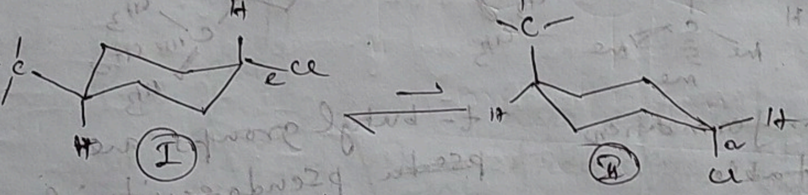
1%

axial conformation of tert-butylcyclohexane (much less stable)

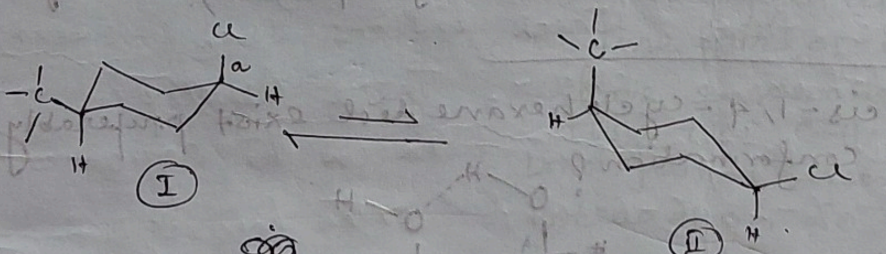
99%

equitorial conformation (much more stable).

The t-butyl group is characterized as "holding group" because ~~of~~ its own tendency to be in the equitorial position holds a smaller substituents axial or equitorial, depending on whether it is cis or trans.



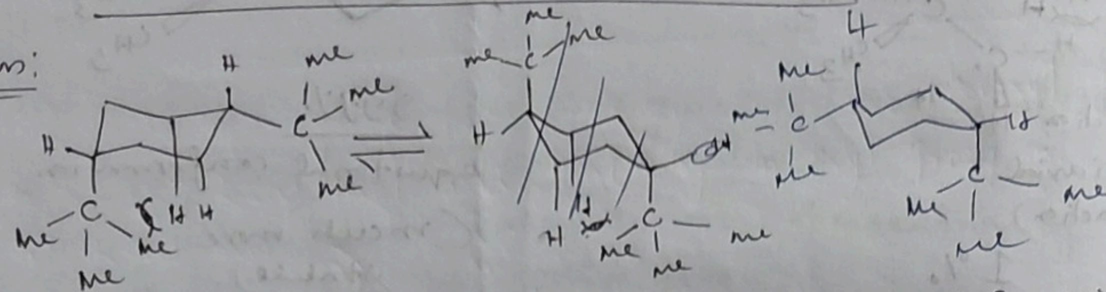
trans-4-t-butylcyclohexane. almost exist in (I) conformation, where t-butyl gr. ~~exist in~~ in equitorial position.



cis-4-t-butylcyclohexane almost exist in (I) conformation where t-butyl gr. in equitorial position & Cl in axial position. As Cl is smaller gr. than t-butyl gr. so it experience less steric hindrance in axial position.

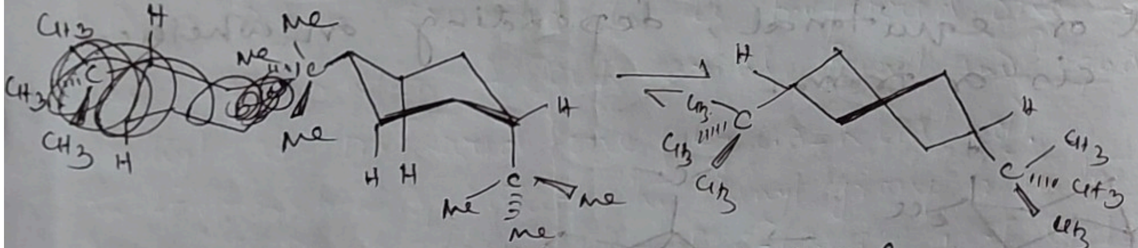
Q which is the most stable conformation of cis-1,4-ditert butylcyclohexane ?

Ans:



Both the chair form is unstable because of excessive steric interaction (1,3- diaxial interaction).

To overcome this steric interaction the molecule assumes a more stable twist boat conformation in which two t-butyl group are so positioned that the strain is minimized.

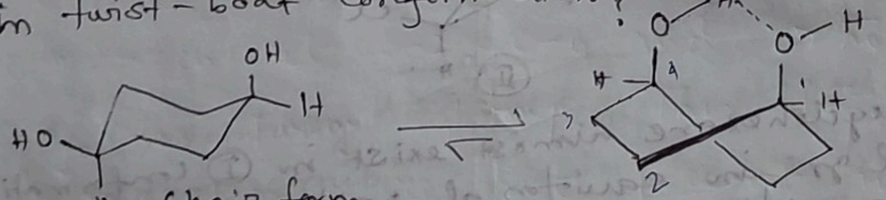


chair conformation less stable

t-butyl groups are ~~pseu~~ pseudo equitorial

~~mo~~ twist boat conformation (more stable and strongly preferred).

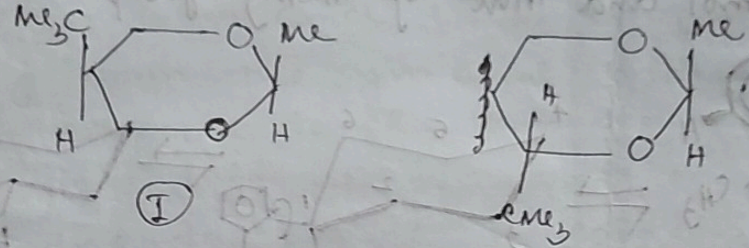
Q Explain why cis-1,4-cyclohexane diol exist preferably in twist-boat conformation?



Chair form
Suffers from 1,3 diaxial interaction

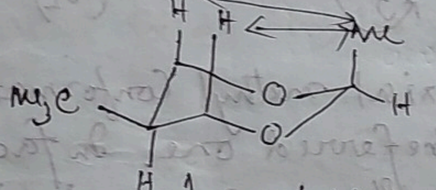
twist boat form
In this form two -OH groups are in hydrogen bonding distance, So intramolecular H-bonding makes the conformation more stable than equitorial form.

Q with cis-2-methyl-5-tert-butyl-1,3-dioxane (I) the conformation with tert-butyl axial is more favoured than the conformation with tert-butyl equitorial — Explain ~~wo~~ and predict what should be the favoured conformation for trans-2-methyl-4-tert butyl-1,3-dioxane (II).



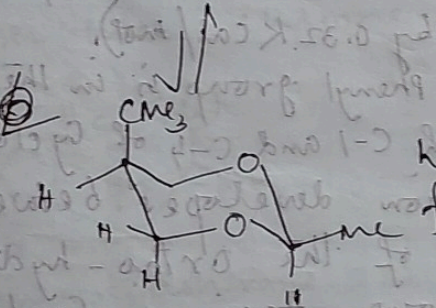
(I)

I can be sketched in chair form as



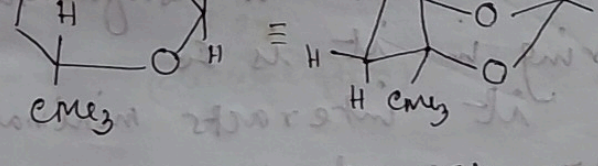
less stable

This form ~~expos~~ is destabilized by syn-axial interaction between CH_3 and H's at C_3 & C_6.

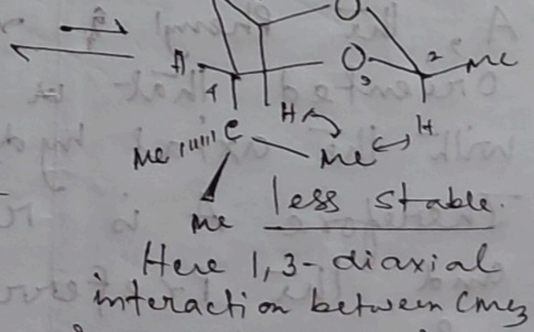


more stable and preferred

here this conformation is free from syn-axial interaction because 1,3 syn axial positions are now occupied by two oxygen atom having lone pair of electrons which have a smaller steric interation than the C-H bond. Lone pair causes no steric interaction. So this conformation is more favoured.



more stable & preferred

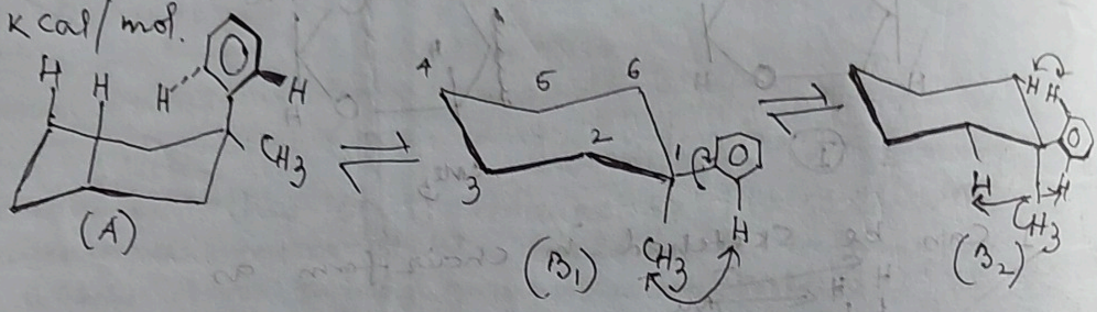


less stable.

Here 1,3-diaxial interaction between CMe_3 & C_2-H & C_6-H is more destabilizing due to large size of t-butyl gr.

Q Predict the most stable conformation of 1- methyl-1 phenylcyclohexane.

The conformational free energy of the Phenyl group is 2.87 Kcal/mol and that of methyl group is 1.70 K cal/mol.



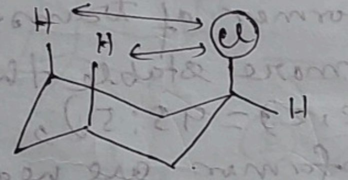
Therefore, equatorial phenyl-axial methyl Conformation (B_1 or B_2) is expected to be Preferred one. In fact, the Conformation A with axial Phenyl and equatorial methyl is Preferred one (by 0.32 K cal/mol).

In Conformation B_1, where the Phenyl group is in the same vertical plane passing through C-1 and C-4 of Cyclohexane chair, a steric interaction developes between the methyl group and one of the ortho-hydrogen atoms of the Phenyl group. Again, in Conformation B_2, where the Phenyl group is nearly in the same average plane (which bisects each C-C bond) of the Cyclohexane chair, there develops serious steric interactions between the equatorial hydrogens at C-2, C-6 and ortho hydrogens of the Phenyl group. This type of steric interaction are not present in Conformation A, the Phenyl ~~g~~ ring in it is so oriented that ~~a~~ it interacts minimally with the axial hydrogens at C-3 and C-5. Therefore A is relatively more stable and the Preferred conformation of 1-methyl-1-Phenyl cyclohexane

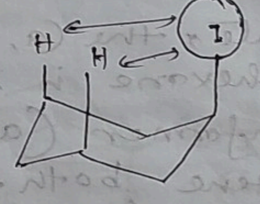
Q Conformational free energy values of Cl and I atoms are almost identical, even though the size of iodine is larger than Cl. Offer an explanation

Since iodine atom is larger than Cl so C–I bond is longer than C–Cl bond. So I remain much away from the syn-axial hydrogens at C_3 & C_5 compared to Cl. Thus steric interaction which is supposed to be increased on going from chlorine to Iodine is compensated by the simultanious increase in distance between the syn-axial hydrogens & the halogen atom.

For this reason the conformational free energy values of Cl (2.68 kJ/mol) and I (2.55 kJ/mol) are almost identical even though the iodine is larger than chlorine.



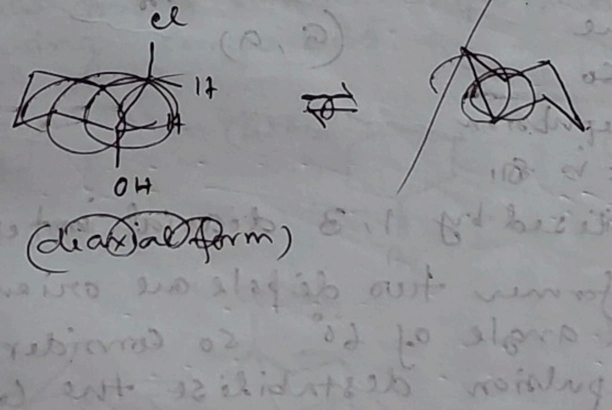
chlorocyclohexane.



Iodocyclehexane

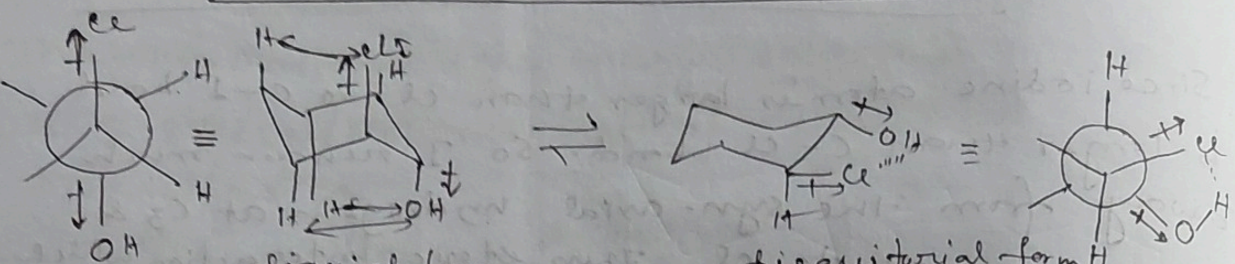
$\Delta(G^\circ_E - G^\circ_A) = -\Delta G^\circ_R$ i,e conformational free energy)

Q Both the conformers of trans-2-chlorocyclohexanol are equally populated — comment.



(diaxial form)

Q Both the conformers of trans-2-Chlorocyclohexanol are equally populated — explain.



diaxial form

diequitorial form

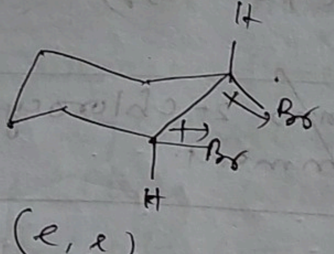
though have no electro static repulsion due to dipoles but it destabilised by 1,3-diaxial interaction

is stabilised through intramoleculor H-bonding but destabilising by electrostatic repulsion between the two dipole.

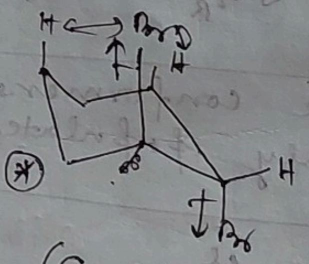
∴ A compromise is reached and two conformers are found to be almost equally populated.

Q In gasius state, the (a, a) conformer of trans-1,2-dibromocyclohexane is much more stable than the (e, e) conformer (a, a : e, e = 95 : 5), but in benzene both the conformer are nearly equally stable (a, a : e, e = 52 : 48). Explain.

Ans :-



(e, e)



(a, a)

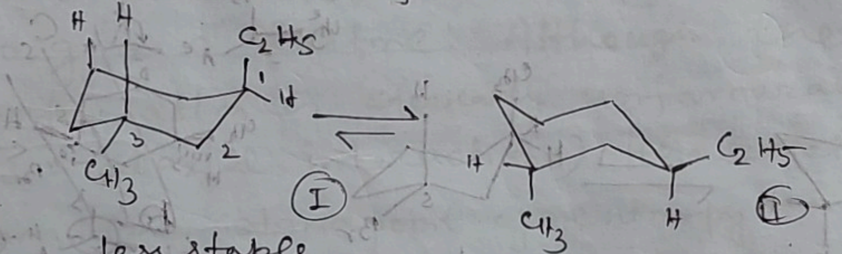
In (a, a)
Here two dipole are oppositely placed so no electrostatic repulsion is acting. But it is slightly destabilised by 1,3 diaxial interaction.
But in (e, e) conformer two dipole are oriented at a dihedral angle of 60°. so considerable electrostatic repulsion destabilise the conformation in comparism to (a, a) conformer.
In gasius state the molecules are well separated so there operate no intermolecular force which may stabilise the (e, e) form.

so, the more stable diaxial form exist predominately. (95:5).

On the other hand, in benzene solution, the molecules come closer to each other and as a result, the electrostatic repulsion between the two dipoles in the diequitorial conformer is minimised due to intermolecular dipole-dipole attraction. Consequently, the two conformers become nearly equally stable and remain almost equally populated (52:48).

Q Which ~~one~~ of the two conformations of ~~tras~~ trans-1-ethyl-3-methylcyclohexane is more stable and why?

Two trans conformers are

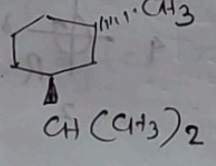


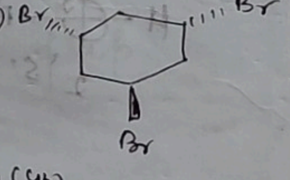
less stable

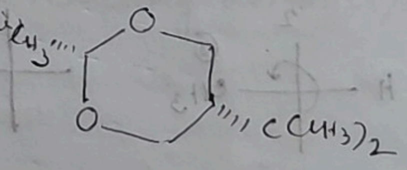
more stable

here 1,3 diaxial interaction is more destabilising because C₂H₅ is a bulkier than methyl group. so ethyl in equitorial position (in II) is more stable.

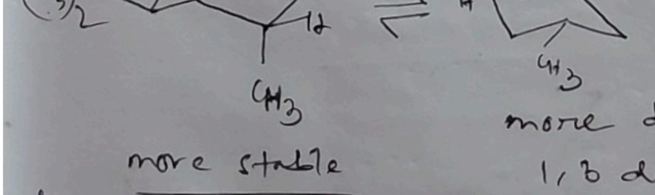
Q Draw more stable conformation for each of the following compounds:

(i)


(ii)


(iii)


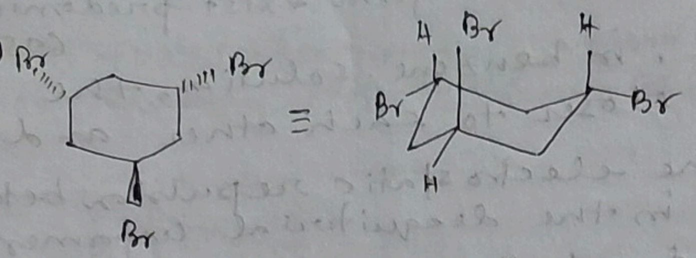
(i)



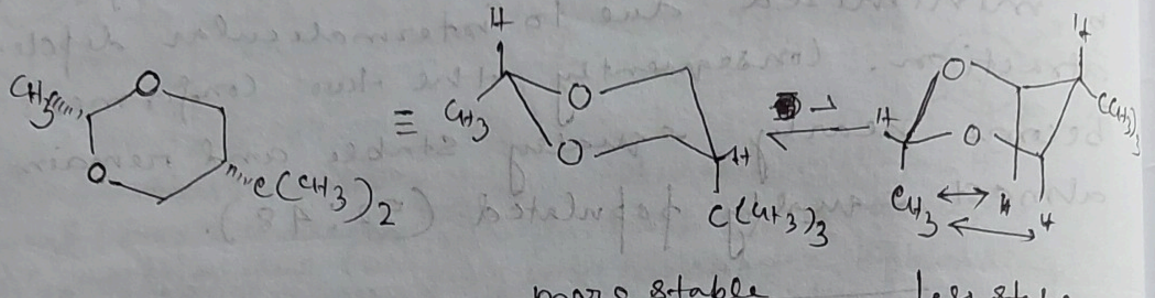
more stable because larger gr. is equitorial.

more destabilising 1,3 diaxial interaction as more bulky gr. is in axial position. so less stable

(ii)

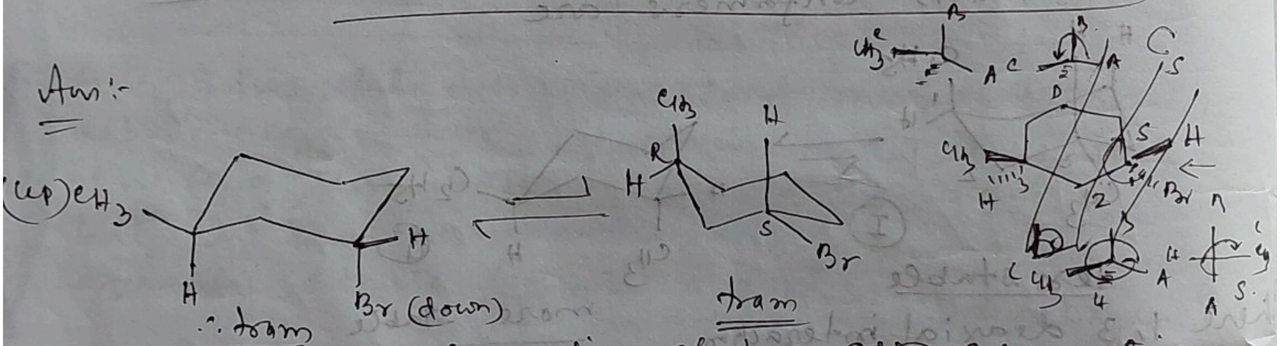


(iii)

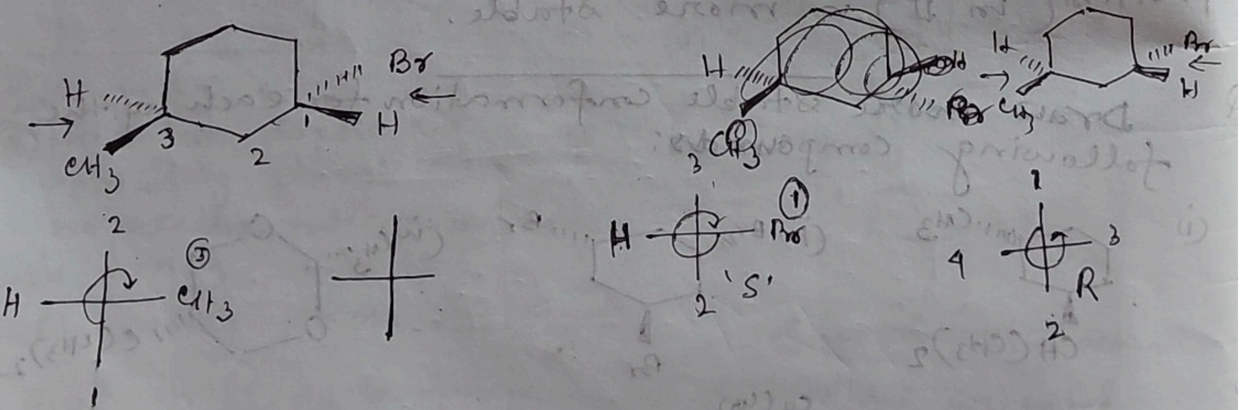


Q Draw the chair conformations of (1S,3R) - 3 - methyl-1 - bromocyclohexane. Predict whether it is a cis or trans - isomer.

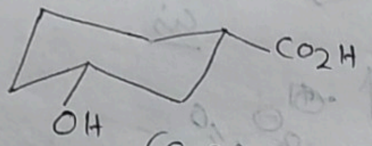
Ans :-



The absolute configaration of the ~~assy.~~ asymmetric carbons remains unchanged after ring flip.

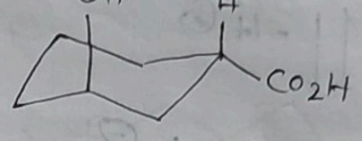


Q. cis-3-hydroxycyclohexanecarboxylic acid readily forms lactone on heating whereas the trans-isomer does not — explain.



(e, e)

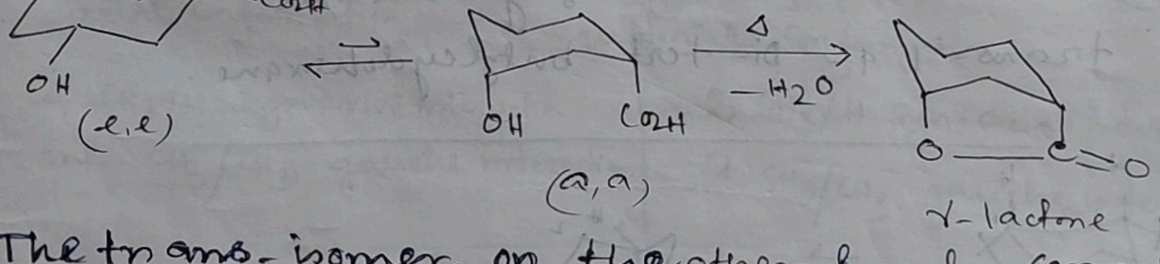
cis-3-Hydroxycyclohexane Carboxylic acid



(e, a)

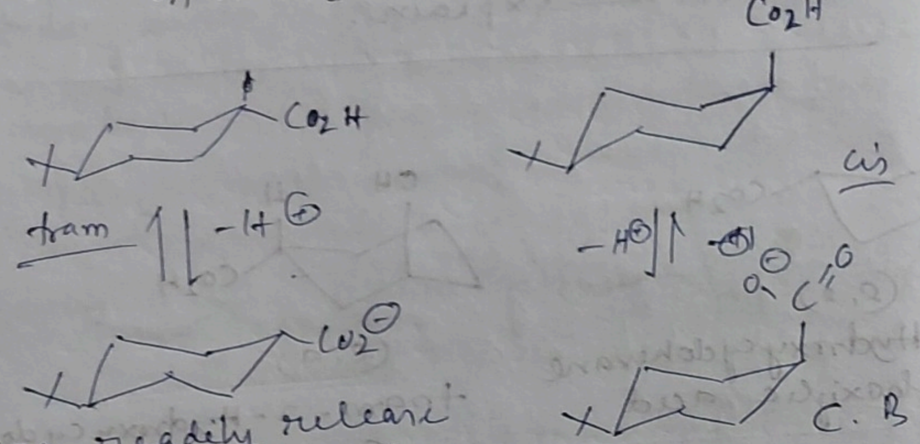
trans-3-Hydroxycyclohexane Carboxylic acid.

The cis-isomer undergoes ready lactonisation on heating through ring inversion process. In the flipped conformation, both the $-CO_2H$ and $-OH$ groups assume syn-diaxial positions and come closer to each other (within reacting distance) to give a lactone. Although the inverted conformation is sterically unfavourable (due to 1,3-diaxial interactions), the reaction is favourable from the standpoint of entropy.



The trans-isomer, on the other hand, cannot form lactone on heating because $-CO_2H$ and $-OH$ groups are far apart (beyond reacting distance), even after ring flip.

Q1 which one of cis and trans 4-t-butyl cyclo hexanecarboxylic acid will act as a stronger acid in water.



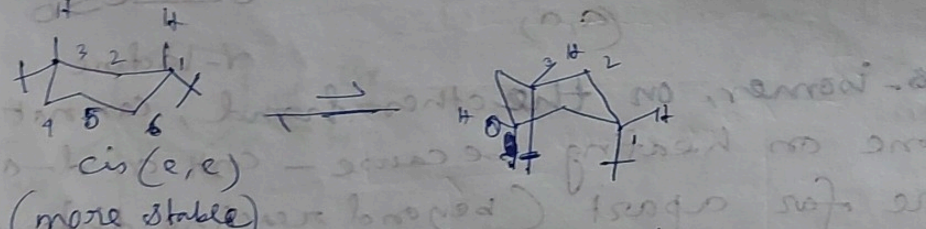
it can readily release $H^{\oplus}$ so it's acidity is greater than cis isomer.

in water the $CO_2^{\ominus}$ will be solvated and bulkiness in axial position increases so 1,3 diaxial interaction increases therefore C.B is less stable than the acid.

Q2 Draw the structure of stable conformation of the following compounds with reasons.

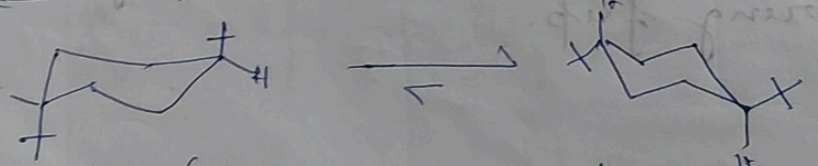
(i) cis-1,3-Di-tert-butylcyclohexane
(ii) trans-1,3-Di-tert-butylcyclohexane
(iii) cis-1,4-di-Tert-butylcyclohexane
(iv) trans-1,4-Di-tert-butylcyclohexane.

(i)



cis (e,e)
(more stable)

(iv)



tram (a,a)

tram (e,e)
(more stable)