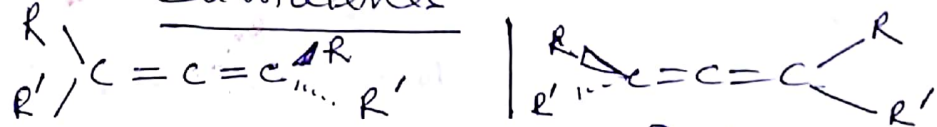
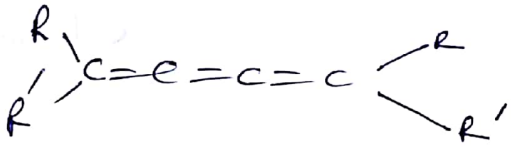
Cumulenes

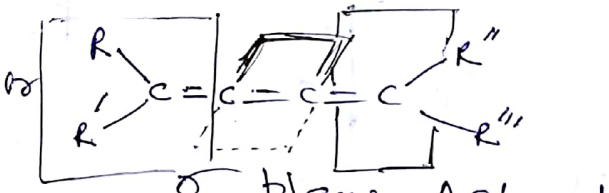
(1) 

Cumulene with even no of double bond where the terminal carbons contain non identical substituents must exhibit optical isomerism (optically active)

(2) Cumulenes with odd no of double bonds instead show E, Z isomerism, because the terminal substituents lie in the same plane due to presence of sp carbon in the middle



σ plane
Achiral

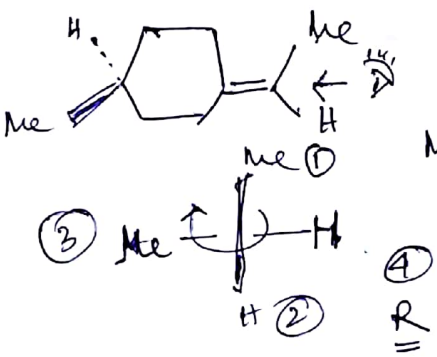


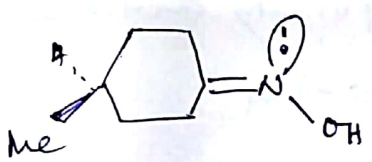
σ plane, Achiral

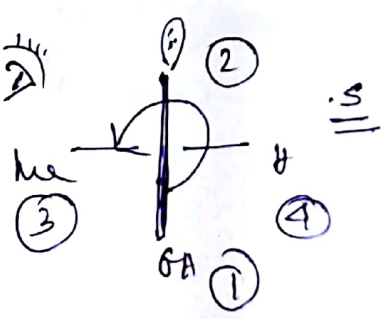
** Unsymmetrically substituted cumulenes with EVEN no of double bonds are chiral (can't show E/Z isomerism) but ODD no of double bonds show E/Z isomerism (can't show chirality).

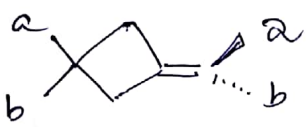
Alkylidenes

Replacement of double bond by a ring (also known as hemispiranes)







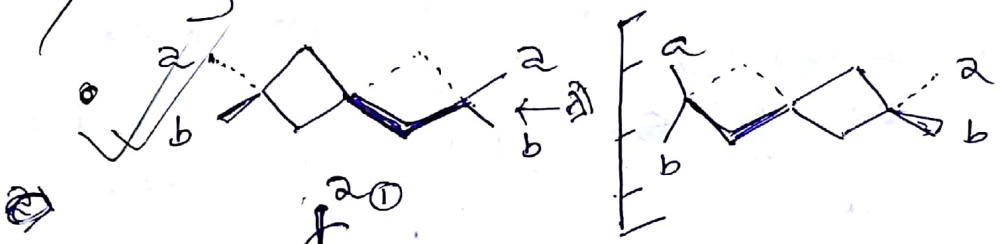


Optically active

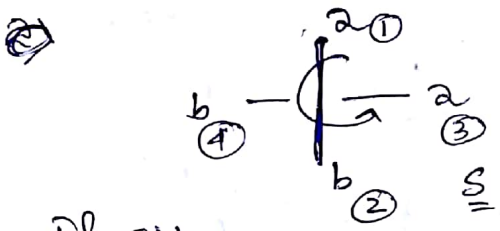
[$a \neq b$ Necessary & Sufficient Condition

Spiranes

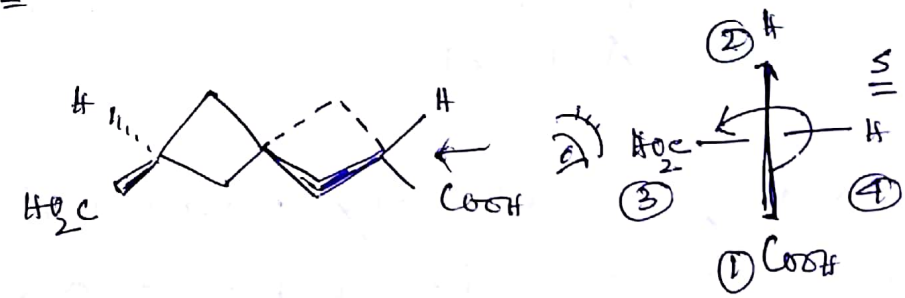
Replacement of both double bonds of allene by rings.



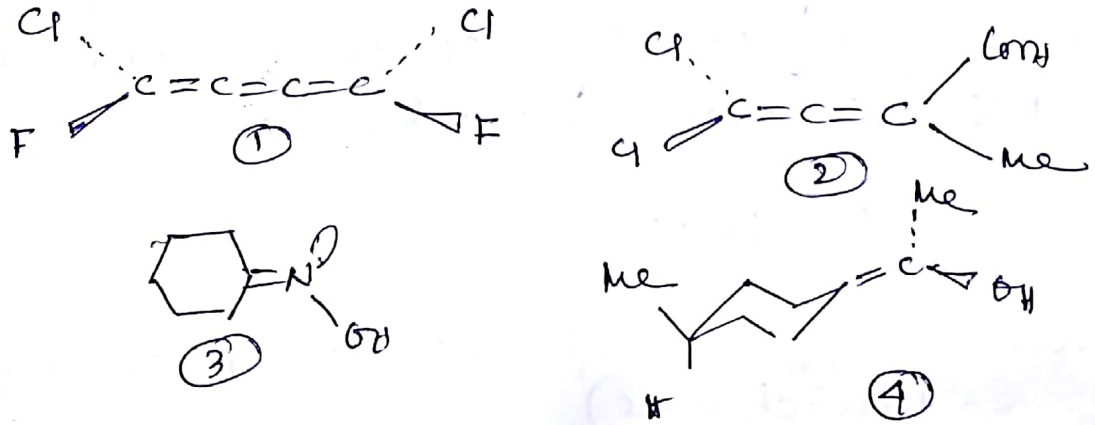
($a \neq b$ necessary & Sufficient for Chirality.



If $a > b$



Q

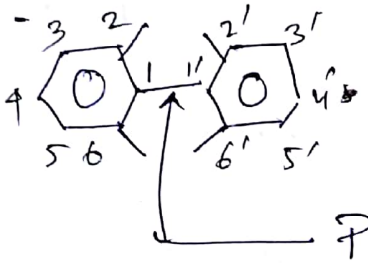


Which is optically active.

Ans Only (4) is active

Atropisomerism

Biphenyls

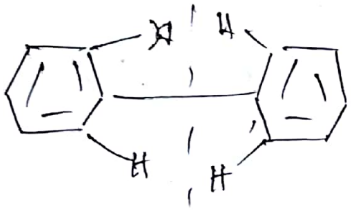


Pivotal bond. (sp^2 — sp^2 σ bond)

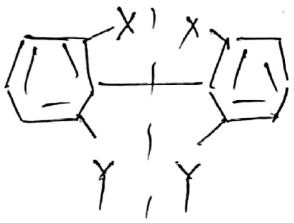
Atropisomer is derived from the greek word "WITHOUT TURNING"

$sp^2 - sp^2$ → σ bond — PIVOTAL BOND

Isolable stereoisomers resulting out of restricted rotation around the pivotal bond. is called ATROPISOMERISM or Torsional isomerism

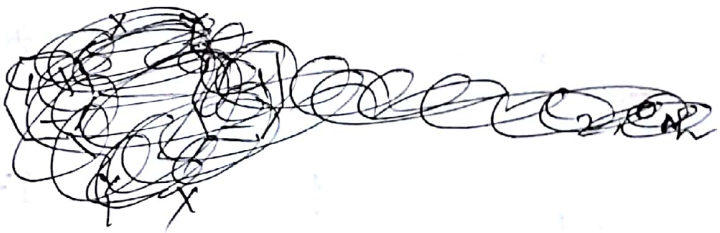


opt. inactive, non resolvable.

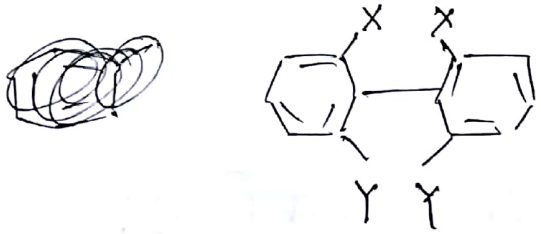


" " " "

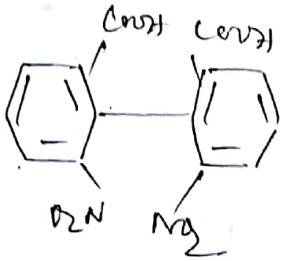
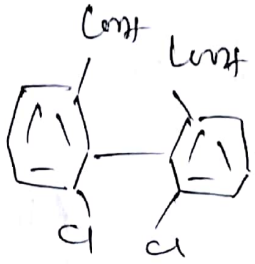
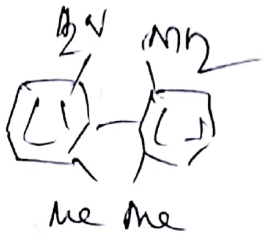
C_2, σ_v



When the ortho substituents are large, rotation around PIVOTAL bond is prevented, Resolution occurs.



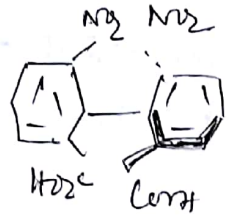
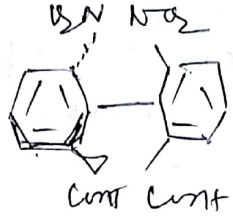
X ≠ Y, opt. active
shows enantiomerism
(atropisomerism)
Resolvable
X & Y are large.

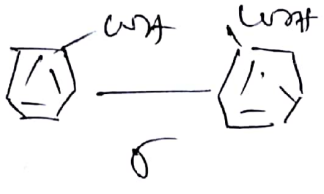
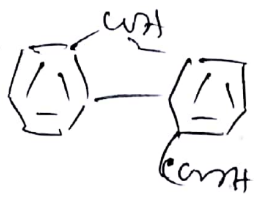
6,6'-dinitrobiphenicaw

6,6'-dichlorobiphenic aw

Two rings can't lie in the same plane.

For showing optical activity, molecule should neither have σ, nor i.

σ = opt. inactive i =

* Torsional angle.

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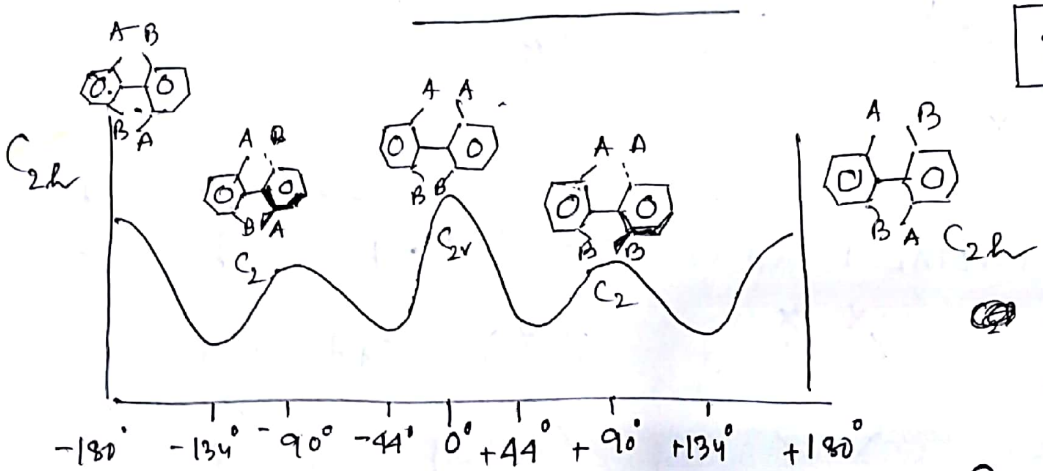
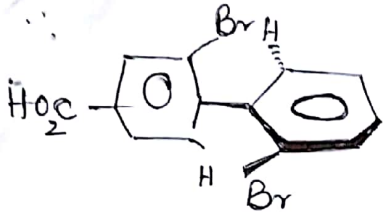


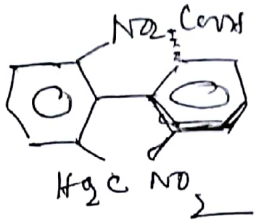
* *
{ A–A, B–B interaction is high energetic than AB, AB interaction

① Stabilisation between π el. overlap } opposing effect
② Steric hindrance

*. Atropisomers are both configurational isomers (as long as their are isolable) since resolvable and also conformational isomers.



Easy racemisation at room temp^r.

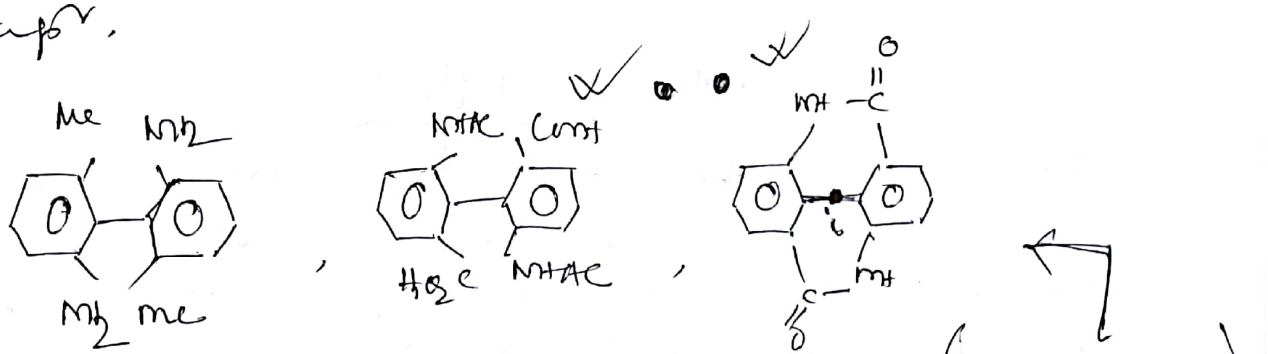


Very high optical stability even at high temp^r.

Racemisation of Chiral biphenyls.

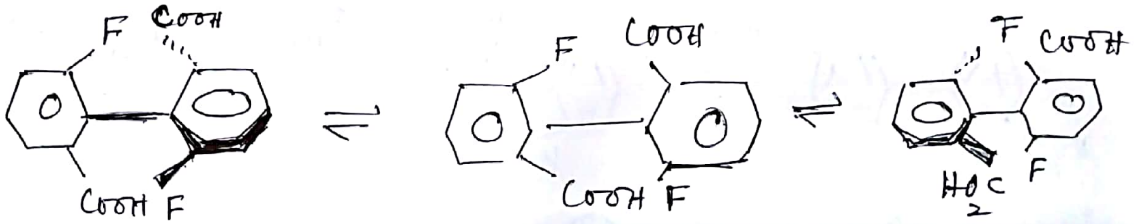
Chirality is due to restricted rotation about pivotal bond ($sp^2 - sp^2$ σ bond).

The two enantiomers having energy barrier of > 80 – 100 kJ/mole are isolable at room temp^r.



a , b , c (Non resolvable)

Resolvable



Chiral form. Achiral plane. Chiral.

Easy racemisation due to presence of small F atoms at ortho position.

It has been found that - interference for free rotation can be minimised by

(i) Bending ~~of~~ H & other substituents
(ii) Compressing C–H (ortho bonds)
(iii) Stretching intramolecular bonds
(iv) Deforming the angle between benzene and interannular bonds.
(v) Deforming benzene rings themselves.

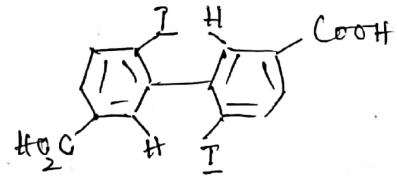
Order of - activation energy for racemisation

$I > Br > CH_3 > Cl > NO_2 > COOH > OMe > F > H$.

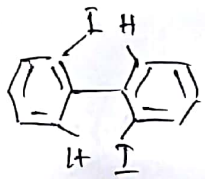
Buttressing Effect -

found that - the activation energy of racemisation for active biphenyls is increased when a substituent is present in meta position to C bond joining the rings. This is called buttressing effect.

Reason: Prevention of outward bending of ortho substituents.

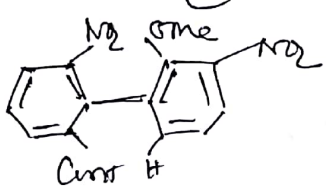


(X)

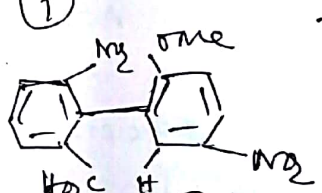


(Y)

$E_{act}(X) - E_{act}(Y) \simeq 21$ K-Cal/mole



(A)

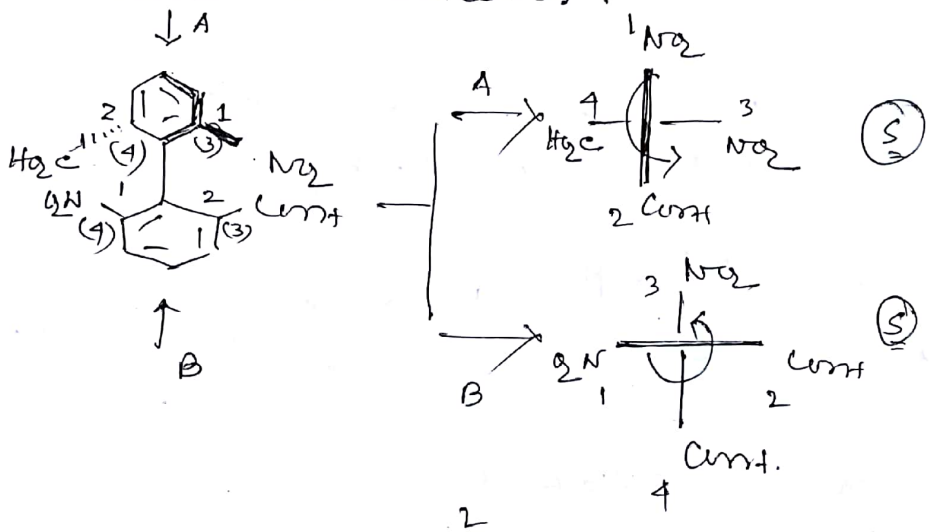


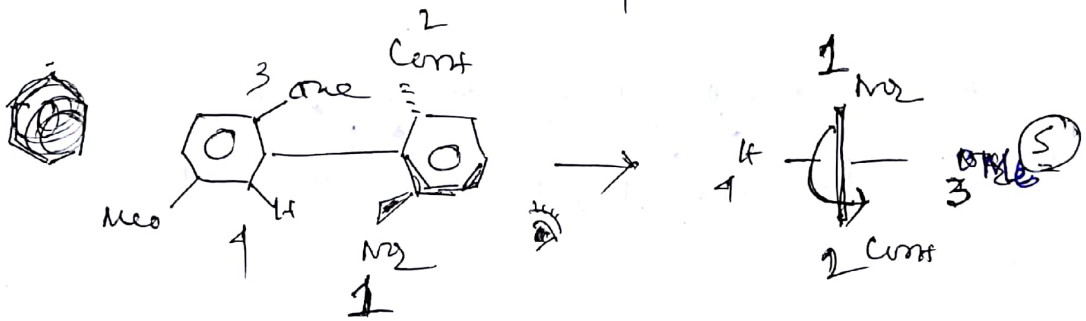
(B)

(B) racemises faster than (A)

Nomenclature

Same as allenes.





P, M descriptors for molecules with Chiral axis

For assigning helical descriptors, only the groups of highest priority nearest to the viewer direction and the far are considered (1 → 3).

If 1 → 3 clockwise it is P (plus) & if anti clockwise it is M (minus).