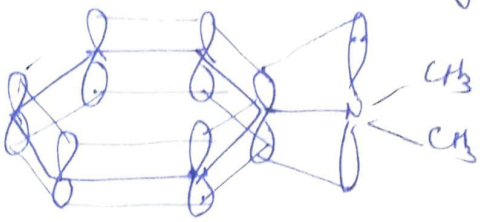
'Steric Inhibition to Resonance'

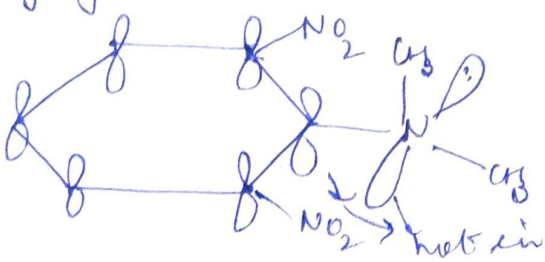
→ For resonance, it is necessary that involved atoms in resonating st. must be coplanar or nearly coplanar for maximum resonance energy (or max. stability).

→ When the involved atoms & orbitals are sterically forced out of planarity, then the resonance is inhibited or reduced, this is c/a steric inhibition of resonance.

eg. In $C_6H_5N(CH_3)_2$, orbitals having lone pair of e^- +ve on N atom is in the plane of benzene ring, hence lone pair takes part in the delocalization



While N, N-dimethyl-2,6-dinitroaniline, NMe_2 gp is out of plane of benzene ring during to +uce of 2 bulky NO_2 gps in vicinity of NMe_2 gp & as a result, lone pair of e^- on N atom of NMe_2 gp can't get delocalized thru lone pair -π conjugation, (π-p conjugation)

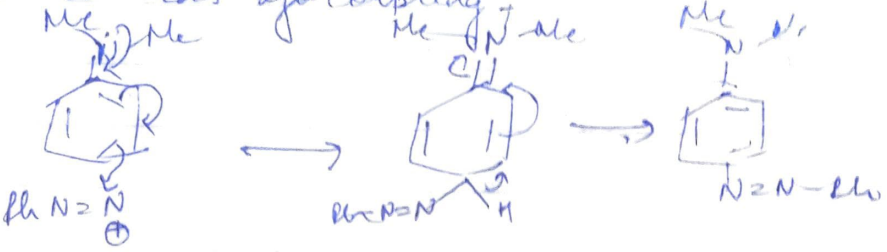


→ not in plane due to steric hind by 2 NO_2 gps

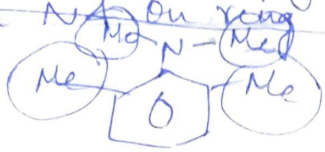
Eg 2) N, N dimethyl aniline & its 2, 6-dialkyl derivatives.

CH_3 gps are much too far away for their bulk

→ NMe_2 gp being e⁻ donating, activates the nucleus towards attack by the diazonium cation $PhN_2^{\oplus}$ i.e. towards azo coupling



2, 6 dialkyl derivative do not couple since two Me gps in o-position to NMe_2, interfere sterically & Me gps attached to N & thus prevent lying in same plane as benzene nucleus, i.e. ~~p orbitals on N~~ on ring Carbon. Thus, it becomes weak $Nu^{\oplus}$ & thus not couples ∴ weak electrophile.

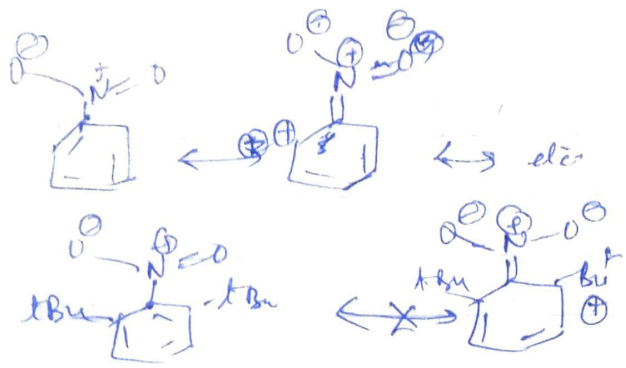


* Steric inhibition of Resonance effects:-

a) Physical Prop. b) Acidity & basicity
c) Reactivity of org. compds.

i) Bond length & B. Strength:-
Due to resonance, –bond achieve partial = bond character & = bond, partial –bond character. But if steric effect inhibits resonance, no such process occurs.

Eg.

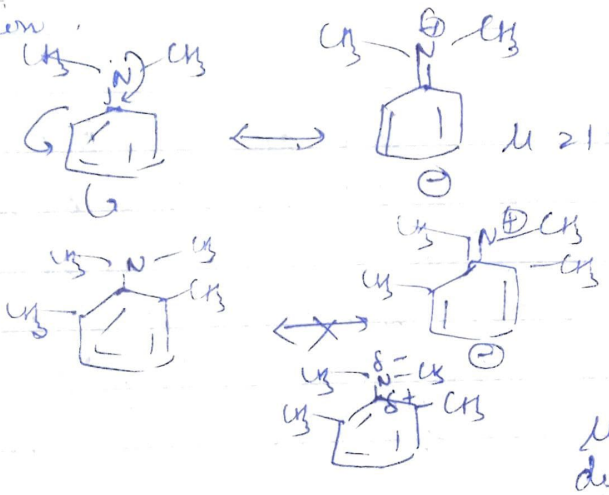


Here partial = bond.

Here C–N bond length is only – bond, & C–N bond strength here less.

2) Dipole Moment :-

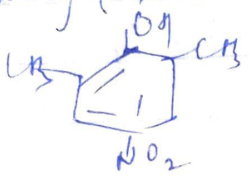
D.M. is lowered due to steric inhibition as distance b/n two poles of such cmpd. is less than that in a cmpd without steric inhibition.



$\mu = 1.61$ D

$\mu = 0.95$ D due to steric inhibition

3) Acidity & basicity :-



More acidic (anion is stabilized due to delocalization & less acidity.

(less acidic)

(NO_2 do not take part in delocalization due to steric inhibition.