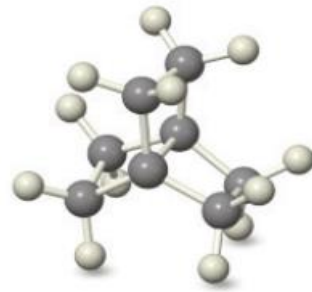
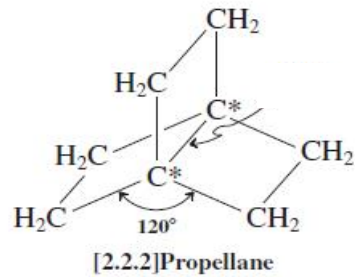
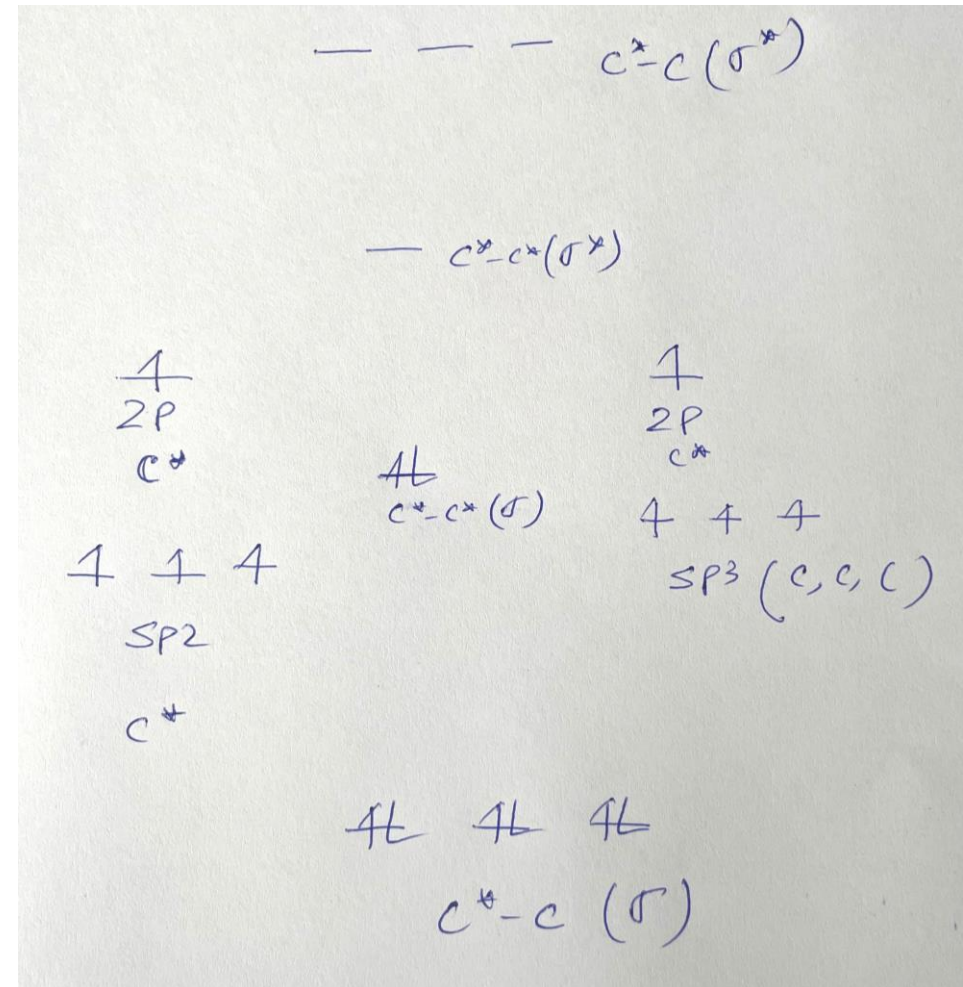


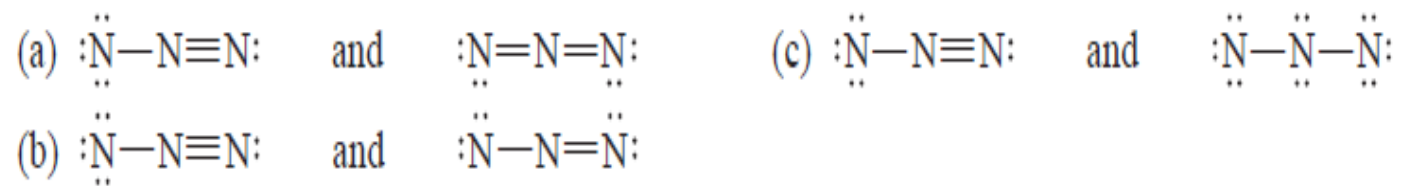
1. The unusual molecule [2.2.2] propellane is shown below. On the basis of the given structural parameters, what hybridization scheme best describes the carbons marked by asterisks? What types of orbitals are used in the bond between them? Draw a MO diagram using hybrid atomic orbitals which describes the bonding of the carbons marked by asterisks (you can show the MOs for any one of the marked carbon atoms). Would you expect this bond to be stronger or weaker than an ordinary C-C single bond?



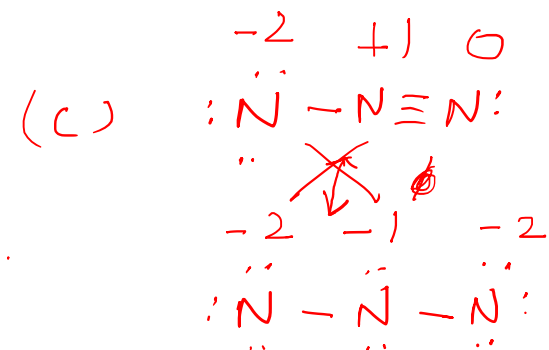
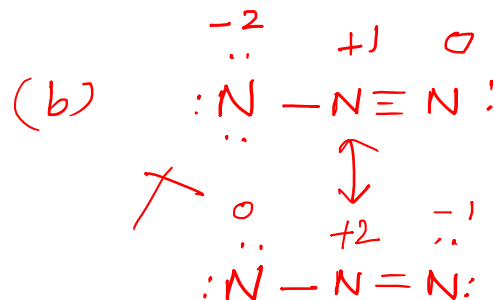
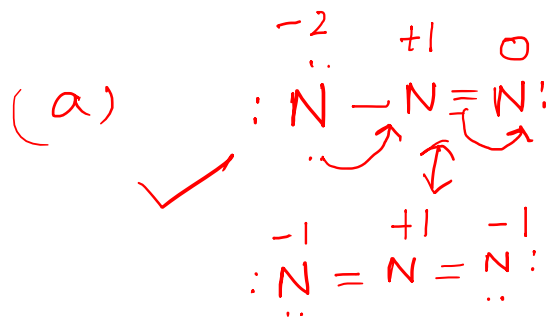
Ans. sp^2 hybridization, p orbitals,
weaker than an ordinary C-C bond.



2. In each of the following pairs, determine whether the two represent resonance contributors of a single species or depict different substances. If two structures are not resonance contributors, explain why.



Ans.

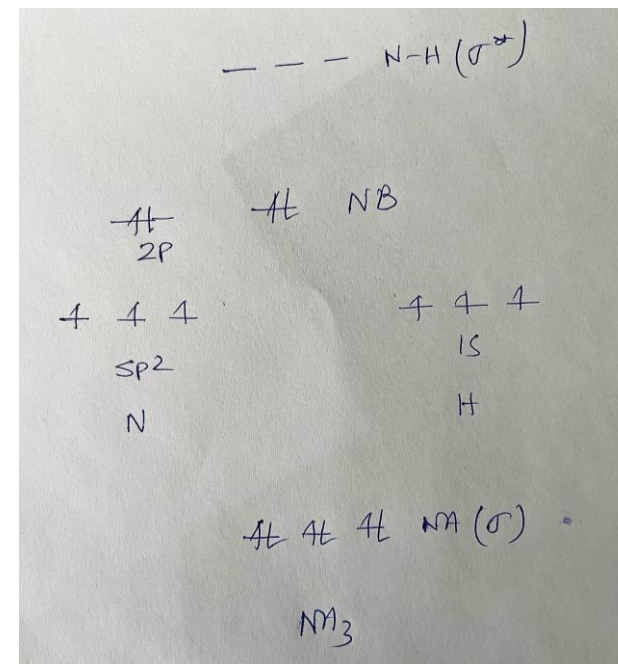


3. Generate the molecular orbitals for planar ammonia, NH_3 (hypothetical).

(a) Show clear diagrams of the atomic orbitals and hybrid atomic orbitals you are using to make the molecular orbitals of planar ammonia. Order the bonding and nonbonding molecular orbitals in terms of energy. Place the appropriate number of electrons in the orbitals.

(b) Between this planar and pyramidal ammonia, which would be more basic? Explain.

Ans. a) In planar ammonia, the nitrogen atom is sp^2 hybridized.



Ans. Since the lone pair in planar ammonia will be in a p orbital, it will be easier to donate than the sp^3 lone pair in pyramidal ammonia

4. Imines are well known derivatives of carbonyl compounds (aldehydes and ketones). Imines are prone to undergo hydrolysis under acidic conditions to produce the parent carbonyl compound as shown below for imine **A**. Based on the MO argument, answer the following questions:

- Why does the protonation happen on nitrogen when **A** is converted to iminium ion **B**? Which MO is involved?
- In the hydrolysis of the iminium ion **B**, the first step is the nucleophilic attack of H_2O . Why does the attack take place at the carbon atom rather than at the nitrogen atom although the latter is actually holding a positive formal charge? Explain based on the relevant MO of the iminium ion. Draw a schematic of this MO.

Ans. a) The lone pairs (non-bonding) on N atom

b) The LUMO (π^*) has more contribution from C

