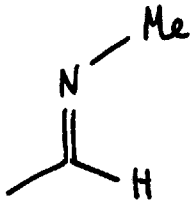
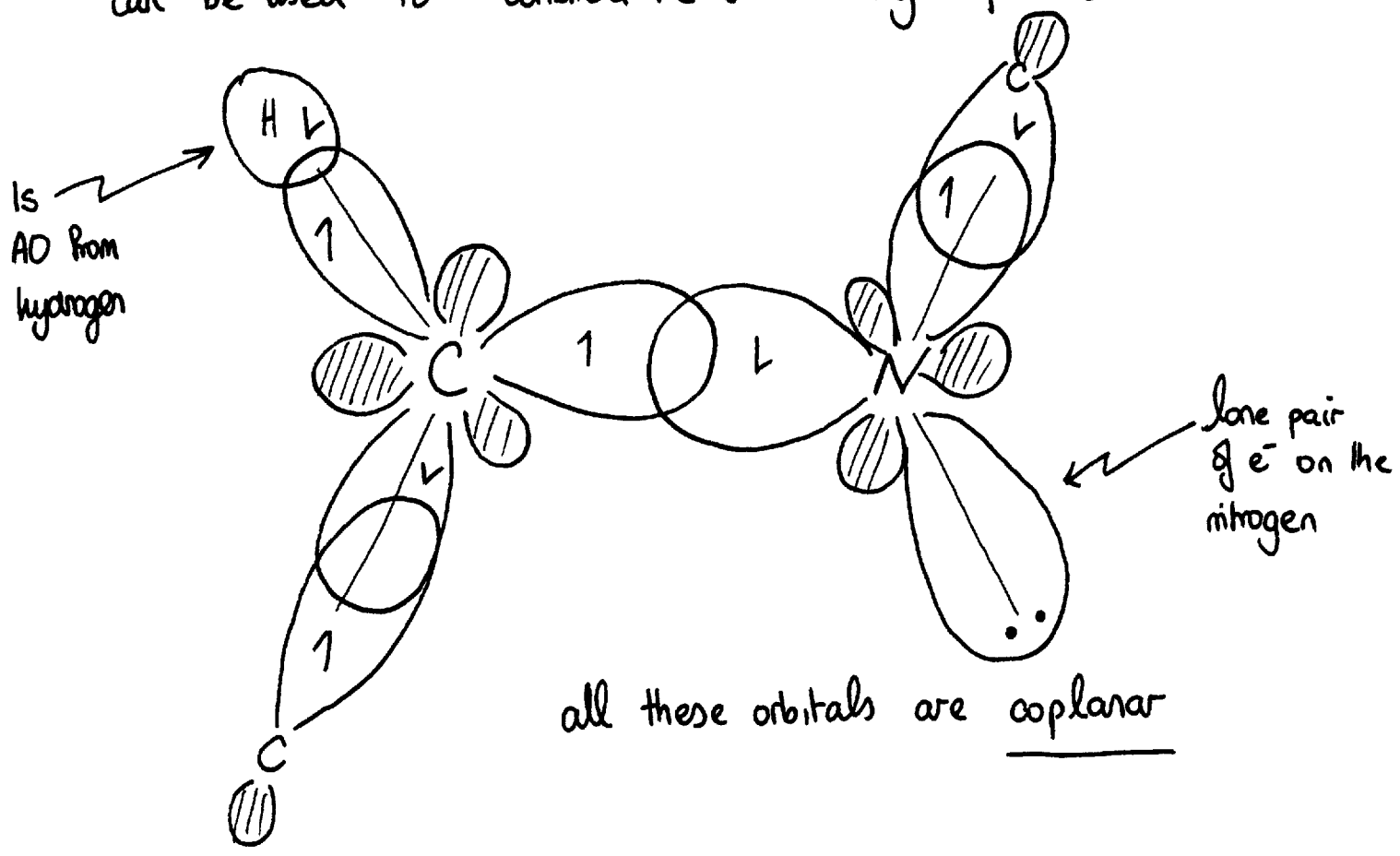
Answer Guide to Problems 1

A molecular orbital picture for the imine functional group.



clearly very closely related to an aldehyde, let's assume the imine Carbon and nitrogen are both sp^2-hybridised.

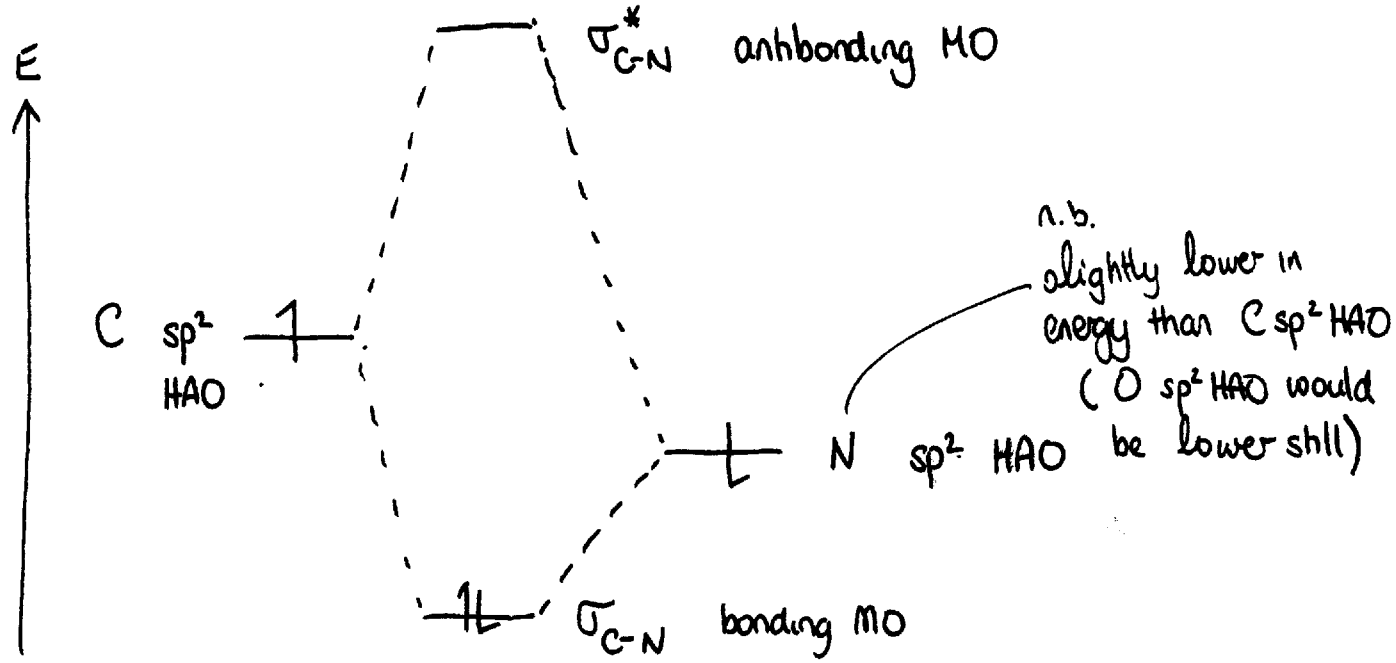
Just as for aldehydes & ketones the three sp^2 hybridised AOs can be used to construct the σ bonding framework.



all these orbitals are coplanar

The previous figure illustrated the σ bonding molecular orbitals in the imine. There are a similar number of antibonding MOs.

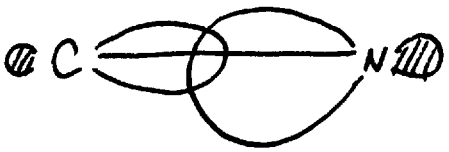
Consider the C — N σ bond:



The C sp^2 HAO & N sp^2 HAO have the correct symmetry to overlap. From the conservation of orbitals, if we overlap two orbitals we must generate two new molecular orbitals, in this case σ_{C-N} & σ^*_{C-N}. Since each sp^2 HAO contributes one e^- each, only the σ bonding MO is populated. This is ∴ an energetically favourable process.

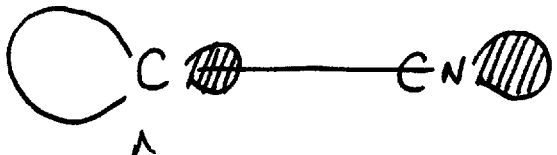
Shape of σ^*_{C-N} & σ_{C-N} in a bit more detail.

σ



drawing larger lobes on the N orbital represents the higher e^- density on N in the MO.

σ^*

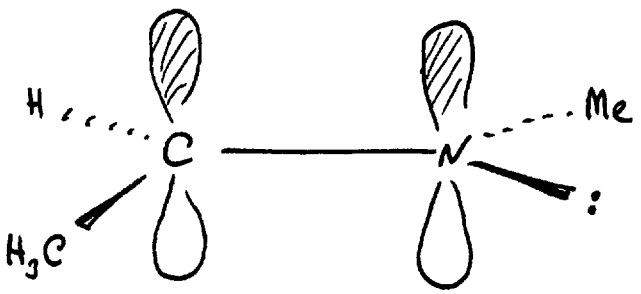


now we see the reverse. the larger lobe is on the C atom. If this orbital were to be populated, more e^- density would reside on the C atom.

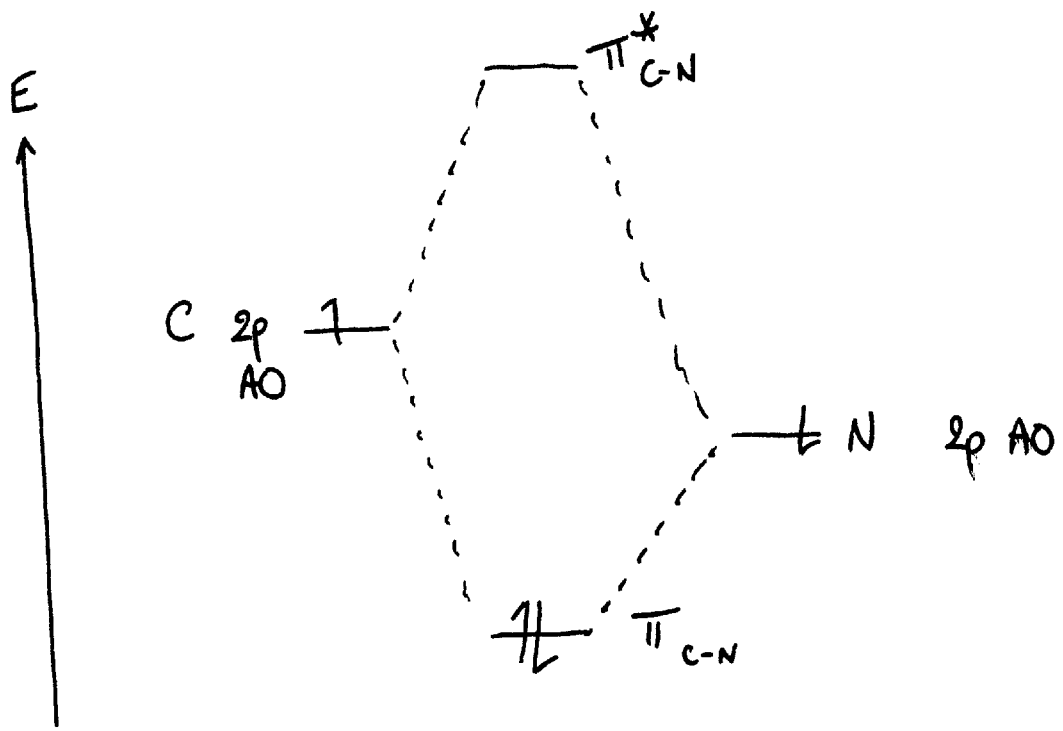
Now for the π bonds: the C & N in our imine have each used all three of their sp^2 HAO's for forming the σ bonding framework (in the case of N, one of the sp^2 HAOs contains the N lone pair - remember Nitrogen has 5 valence e^-).

C & N has one pAO each remaining for bonding. The pAO is orthogonal to the plane containing the σ bonding framework.

ie

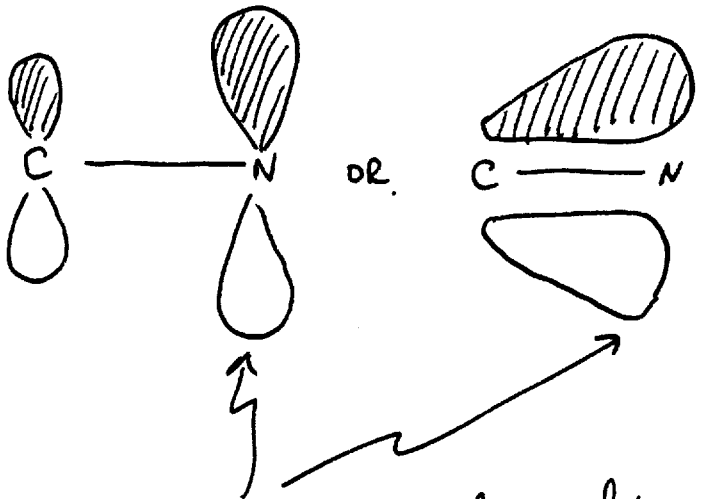


Both pAO's have the correct symmetry to overlap:



Again note that two p AOs overlap (or mix) to generate two new MOs, namely the π & π^* MOs. Once again we have two e^- (one from each atom) & ∴ only occupy the lower energy π MO; thus this orbital overlap is also an energetically favourable process.

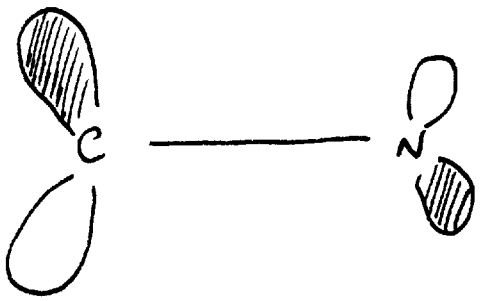
Shape of π bond :



Note the lateral overlap of p AOs generates a π MO in which there is zero probability of e^- in this MO occurring in the plane that contains the σ bonding framework.

once again the larger lobe or bulge on N represents ↑ed e^- density at the N centre (N is more electronegative than C).

& for the π^* MO



Again if π^* were to be populated there would be more e^- density on the Carbon.

Just as for the C=O group in aldehydes & ketones etc, the important (frontier) MO's are π & π^* in imines.

So why are imines less electrophilic than aldehydes & ketones

cf. the electronegativity of C 2·55 (Pauling scale)

N 3·04

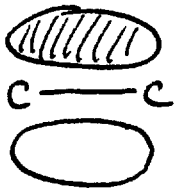
O 3·44

These values show that oxygen is far more "electron withdrawing" than nitrogen. Thus the C=N bond will be appreciably less polarised than C=O ie there will be less δ^+ charge on an imine C than on an aldehyde Carbon

This is reflected in the π MO s :

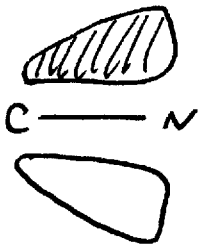
Pictorially:

C = C



No polarisation in a C=C

$\overset{\delta^+}{C} = \overset{\delta^-}{N}$



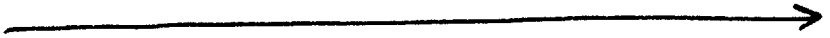
π bond polarised

$\overset{\delta^+}{C} = \overset{\delta^-}{O}$

π bond even more strongly polarised rendering the carbonyl carbon the least e^- deficient & ∴ most susceptible to nucleophilic attack.

Q2

$C=O$ $C=S$ $C=Se$



decreasing bond strength.

lots of ways to think about this. Let's just consider the $\pi_{C=O}$, $\pi_{C=S}$ & $\pi_{C=Se}$ bonds (the same rationale can be applied to the corresponding σ bonds).

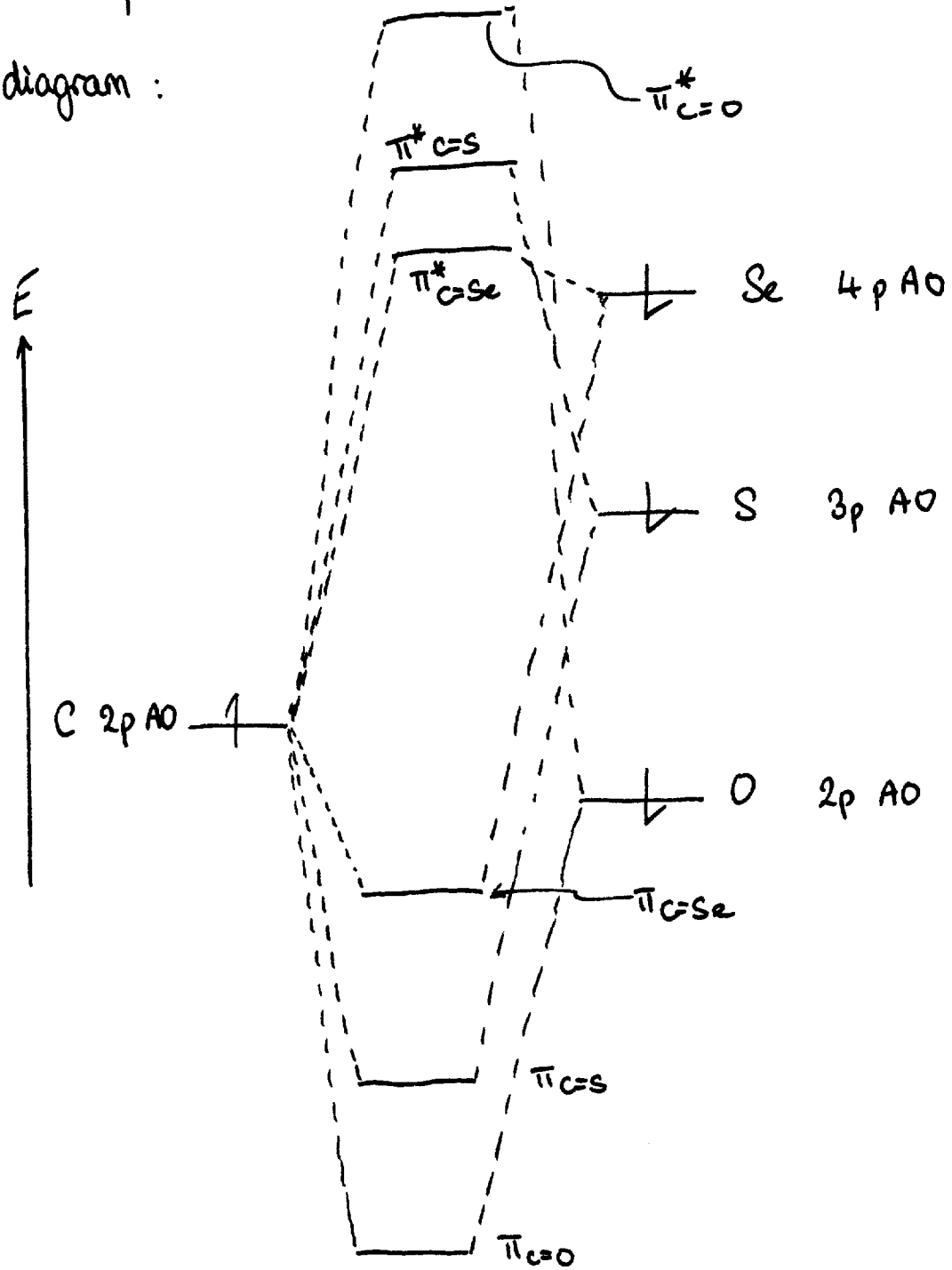
$\pi_{C=O}$ formed by C 2p AO overlapping with O 2p AO

$\pi_{C=S}$ C 2p AO —— " —— S 3p AO

$\pi_{C=Se}$ C 2p AO —— " —— Se 4p AO.

In general, the better is the degree of orbital overlap the greater is the degree of stabilisation. Orbitals that are similar in size and energy overlap the most efficiently & ∴ lead to the greatest degree of stabilisation.

Let's place all three π bonds on the same MO energy diagram :



In every case orbital overlap leads to an energetically favourable interaction. However the greatest degree of stabilisation arises from the most efficient orbital overlap

..., that is from the orbitals that are closest in energy

& one is 2pC with 2pO. - net result C=O is the most stable & ∴ strongest bond.

Another way of thinking about this is to consider the energy that would need to be put into the system in order to break the bond & bring the system back to its original state.