OUTLINE ANSWER

2. (a) (i) The cis isomer is preferred (i.e. lower in energy). Although the trans isomer should be favoured by both steric and dipole arguments the dominant factor is the operation of two anomeric effects between the lone pairs on nitrogen ($n_{Nsp2}$) and the anti-periplanar $\sigma^*_{N-F}$ orbitals.

(ii) The gauche conformer is preferred (i.e. lower in energy). Both conformers are staggered and so minimise dihedral angle strain. The anti conformer is favoured by dipole effects but the dominant factor is the operation of 2 anomeric effects between the lone pails on the nitrogen ($n_{Nsp3}$) and the anti-periplanar $\sigma^*_{N-H}$ orbitals.

(b) The stretching frequency of the carbonyl bond reflects the strength of that bond. This can be correlated with the degree of double bond/single bond character is has. From consideration of resonance diagrams showing $n_{Np} \rightarrow \pi^*_{C=O}$ resonance it is clear that the stronger this overlap is less the double bond character and the weaker the $C=O$ bond is. For the lactam on the left the nitrogen can adopt a close to $Sp^2$ hybridisation such that the lone pair in the p-orbital can overlap well with the $\pi^*_{C=O}$ orbital – consequently the carbonyl is weak [$v(C=O) 1680 \text{ cm}^{-1}$]. For the lactam on the right the nitrogen is at a bridgehead and consequently is pyrimadilised (~$sp^3$). Moreover, the geometry is such that this ~$sp^3$ N-lone pair cannot align with the $\pi^*_{C=O}$ orbital. Overlap is therefore poor – consequently the carbonyl is strong [$v(C=O) 1750 \text{ cm}^{-1}$].

(c) The axial C-Cl bond is longer because the $\sigma^*$ orbital of this bond participates in an anomeric effect with the anti periplanar axial lone pair ($n_{Osp3}$) on the adjacent ring oxygen. The equatorial C-Cl bond cannot because the only anti periplanar donor to the $\sigma^*_{C-Cl}$ is a $\sigma_{C,O}$ bond, which is a poor donor:
(d) (i) Protonation of one of the hydroxyl groups initiates a pinacol rearrangement:

![Pinacol rearrangement diagram](image1)

1) $\pi^*_{\sigma_C}$

2) $\sigma_{C-C}$

(ii) The diazomethane undergoes 1,2-addition to the carbonyl setting up a Tiffaneau-Demyanov semi-pinacol rearrangement:

![Tiffaneau-Demyanov rearrangement diagram](image2)

1) $\pi^*_{\sigma_C}$

2) $\sigma_{C-C}$