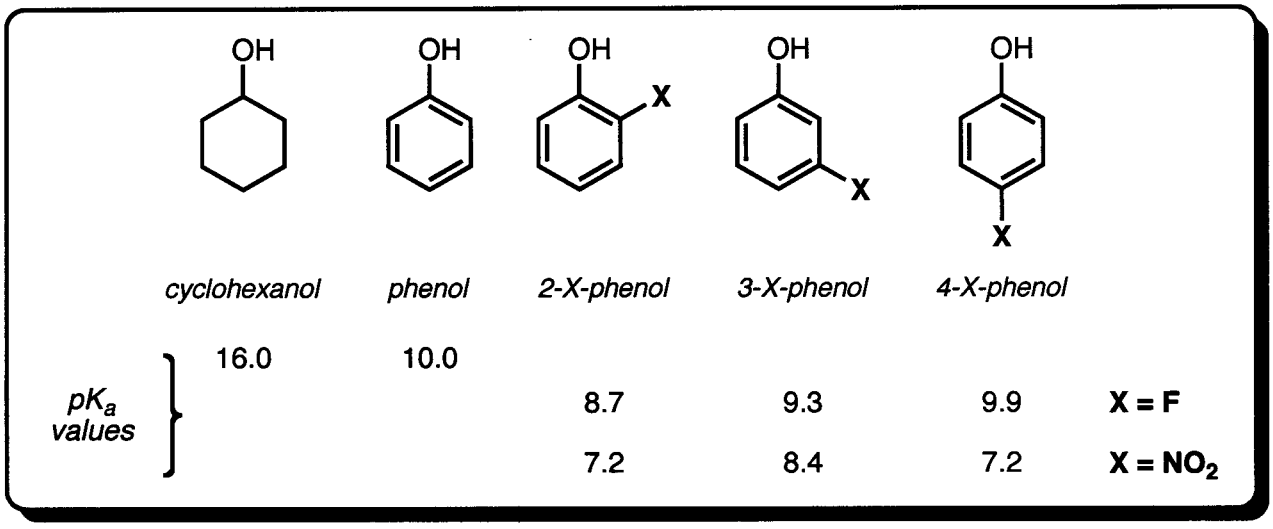
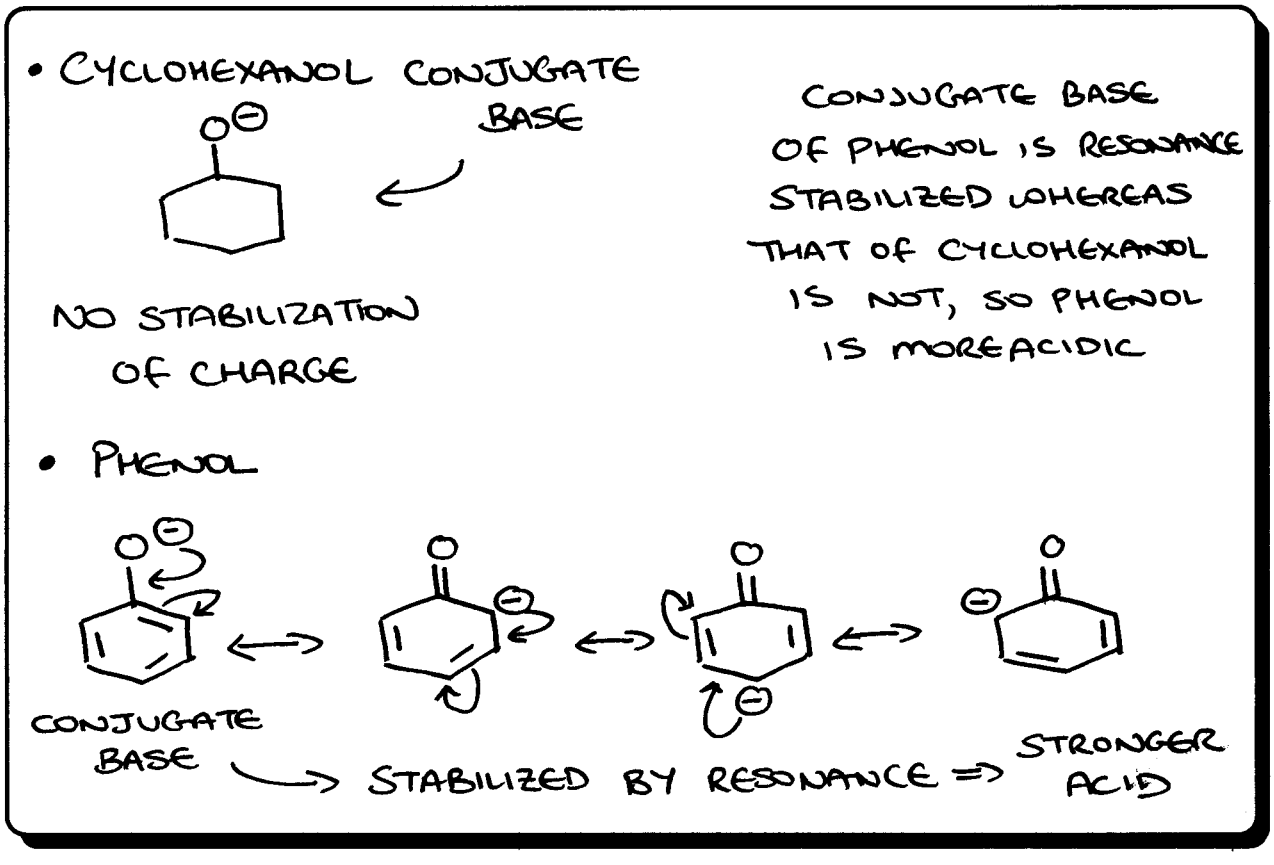
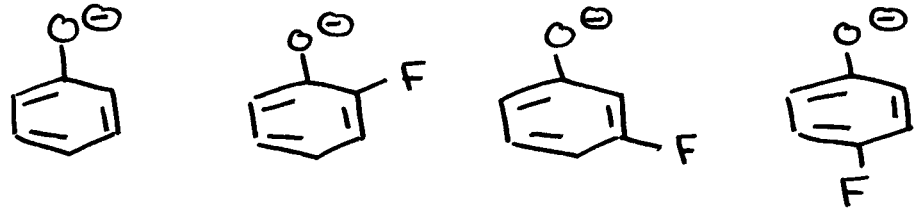
Q5. In the box below, you are given the pK_a values for a series of compounds, the least acidic is cyclohexanol (pK_a = 16.0). The pK_a value for phenol is 10.0, and two series of substituted phenols are given: 2-fluorophenol, 3-fluorophenol, and 4-fluorophenol have pK_a values of 8.7, 9.3, and 9.9, respectively; 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol have pK_a values of 7.2, 8.4, and 7.2, respectively. Note: both –F and $-NO_2$ are strong electron withdrawing groups.



(a) Briefly explain (using words AND illustrations) why phenol is (literally and actually!) a million times more acidic than cyclohexanol (5 points).



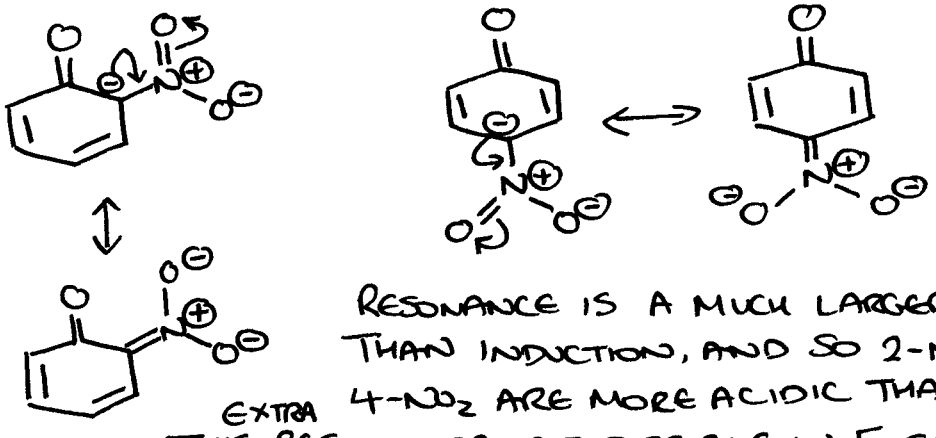
(b) Briefly explain (using words and illustrations as you feel necessary) the trend observed in the acidity of 2-, 3-, and 4-fluorophenol (5 points).



EACH STRUCTURE IS STABILIZED BY RESONANCE, AND THERE IS AN INDUCTIVE EFFECT (THAT ALSO STABILIZES THE ANION) THAT RESULTS FROM THE ELECTRONEGATIVE F ATOMS. THE CLOSER THE F TO THE O^-, THE BIGGER THE INDUCTIVE EFFECT, SO 2-F IS MORE ACIDIC THAN 3-F, WHICH IS MORE ACIDIC THAN 4F

(c) Briefly explain and illustrate why the trend observed in the acidity of 2-, 3-, and 4-nitrophenol is different to that observed for the analogous series of phenolic compounds containing fluorine (5 points).

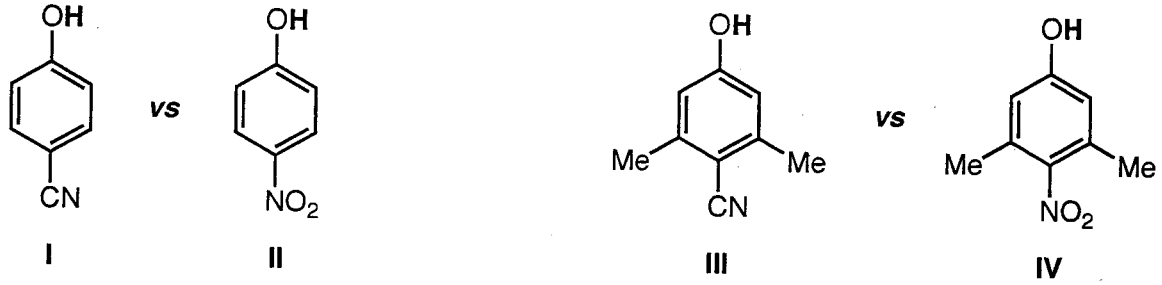
WITH THE NO_2 GROUP IN THE 2- AND 4- POSITIONS, EXTRA RESONANCE STABILIZATION IS POSSIBLE, AND THIS DOES NOT HAPPEN IN THE 3- POSITION



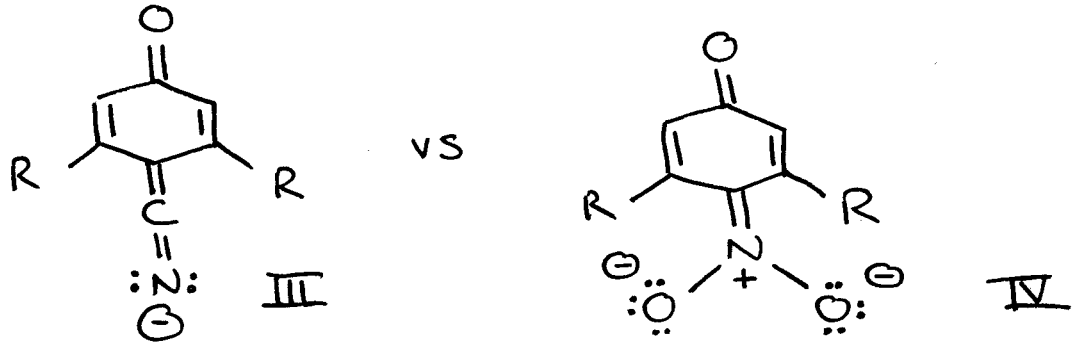
RESONANCE IS A MUCH LARGER EFFECT THAN INDUCTION, AND SO 2-NO_2 and 4-NO_2 ARE MORE ACIDIC THAN 3-NO_2

EXTRA RESONANCE NOT POSSIBLE IN F SERIES

EXTRA CREDIT. The pK_a values for 4-cyanophenol (**I**) and 4-nitrophenol (**II**) are approximately the same, i.e., the phenolic protons (**bold**) in each of these compounds are equally acidic. In contrast, however, the dimethyl-substituted compounds differ significantly in their acidity; the dimethyl-cyano compound (**III**) is much more acidic than the dimethyl-nitro compound (**IV**). Explain (using both words and drawings as you feel appropriate) this observation in the box below. (15 points) Hint: think resonance...



ALL OTHER RESONANCE CONTRIBUTORS BEING APPROXIMATELY EQUAL, CONSIDER THE FOLLOWING:



WHEN R = H, BOTH CONTRIBUTORS ARE OK, BUT WHEN R = Me, STERIC INTERACTIONS BETWEEN THE Me GROUPS AND THE OXYGEN ATOMS IN IV DISFAVOR THIS RESONANCE CONTRIBUTER. THE CN GROUP DOES NOT SUFFER FROM THIS PROBLEM AS IT IS LINEAR (NO_2 IS TRIANGULAR) AND SO III IS MORE ACIDIC THAN IV