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.

\[
\begin{array}{cccc}
\text{cyclohexanol} & \text{phenol} & \text{2-X-phenol} & \text{3-X-phenol} & \text{4-X-phenol} \\
\text{pK}_a \text{ values} & 16.0 & 10.0 & 8.7 & 9.3 & 9.9 & 7.2 & 8.4 & 7.2 \\
\end{array}
\]

\(X = \text{F}\)

\(X = \text{NO}_2\)

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

- Cyclohexanol conjugate base:
  - **No stabilization of charge**

- Phenol:
  - Conjugate base of phenol is resonance stabilized whereas that of cyclohexanol is not, so phenol is more acidic.
(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 4-F.

(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\(_2\). This resonance not possible in F series.
EXTRA CREDIT. The pKₐ 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 contributor. The CN group does not suffer from this problem as it is linear (NO₂ is triangular) and so III is more acidic than IV.