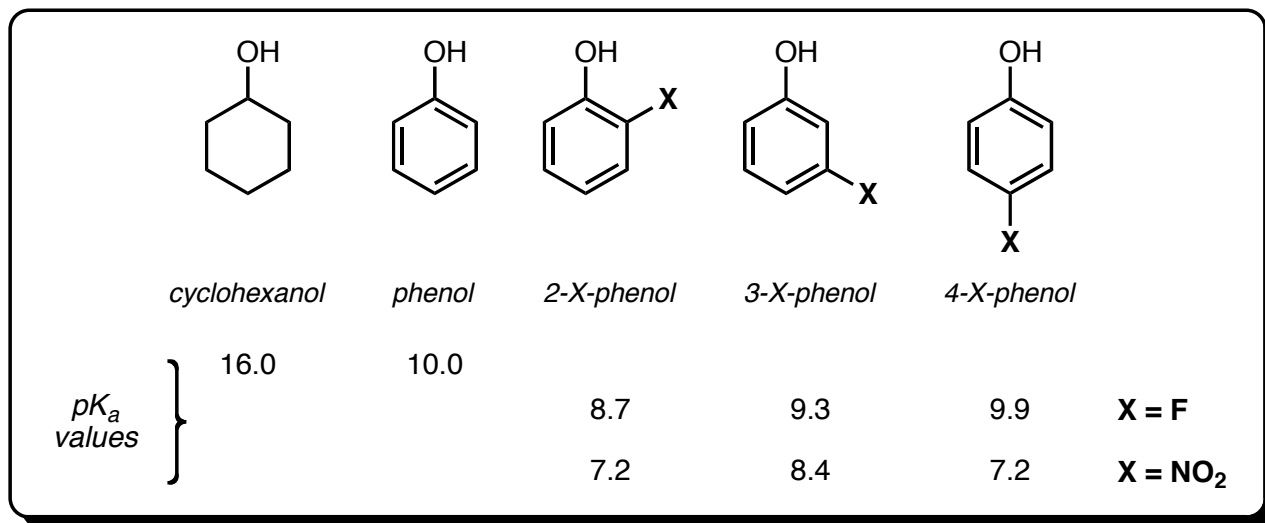


Q5. In the box below, you are given the  $pK_a$  values for a series of compounds, the least acidic is cyclohexanol ( $pK_a = 16.0$ ). The  $pK_a$  value for phenol is 10.0, and two series of substituted phenols are given: 2-fluorophenol, 3-fluorophenol, and 4-fluorophenol have  $pK_a$  values of 8.7, 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.

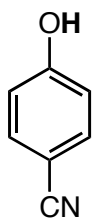


(a) Briefly explain (using words AND illustrations) why phenol is (literally and actually!) a million times more acidic than cyclohexanol (5 points).

(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).

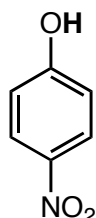
(c) Briefly explain and illustrate why the trend observed in the acidity of 2-, 3-, and 4-nitrophenol is different to that observed for the analogous series of phenolic compounds containing fluorine (5 points).

**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...

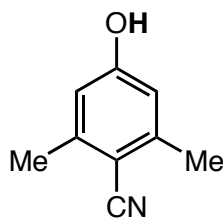


**I**

vs

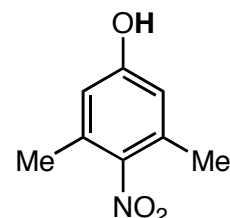


**II**



**III**

vs



**IV**

Empty box for the student's explanation.