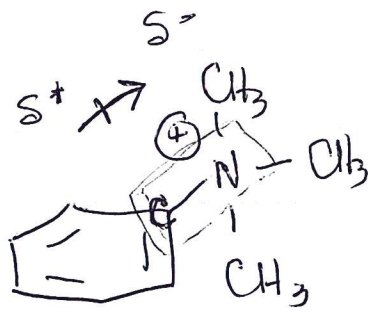
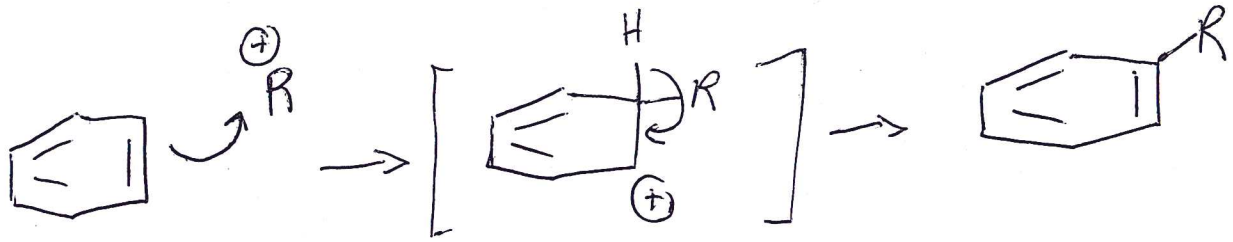
16.40



The N,N,N-trimethyl ammonium group is an electron-withdrawing group by INDUCTION, not resonance.

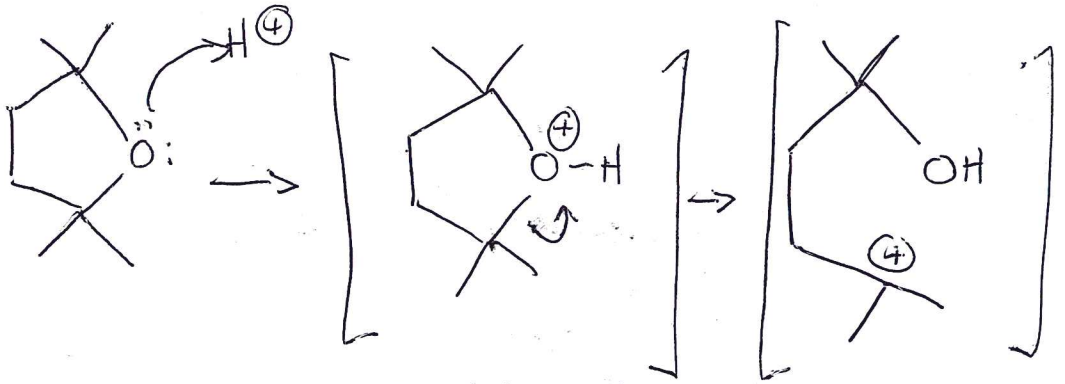
The C-N bond between the benzene parent and positively charged N atom is polarized toward the N atom. The N pulls ⊖ out of the ring to "try" and get ⊖ back and neutralize the ⊕ charge.

16.64 This reaction is a variation on the Friedel-Crafts alkylation. The F-C alkylation is a reaction between benzene and a carbocation.



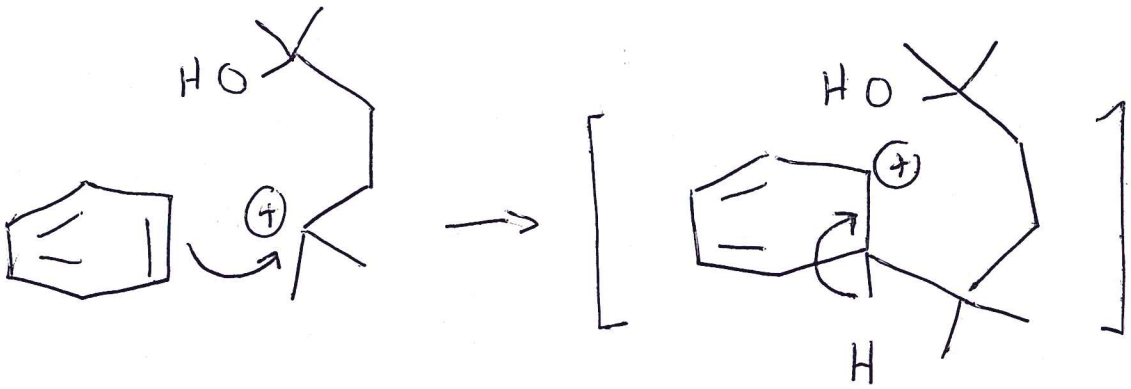
16.64 (cont'd)

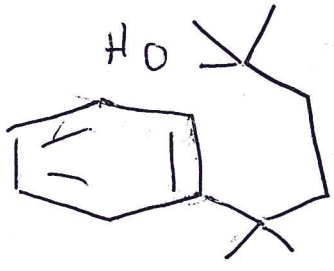
The carbocation for this reaction is derived from reaction of 2,2,5,5-tetramethyltetrahydrofuran and sulfuric acid



OXONIUM ION

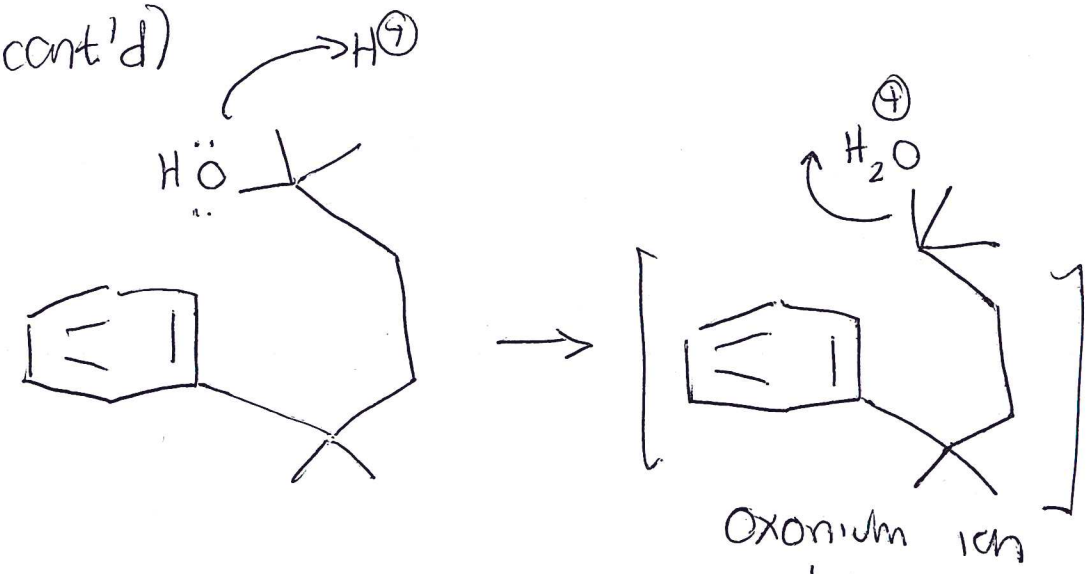
This carbocation can then react with the benzene to "start" the FC reaction





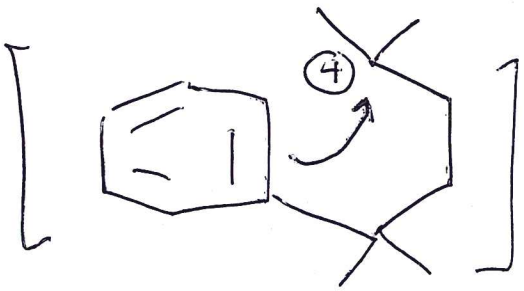
This 3° alcohol then continues to react

16.64 (cont'd)



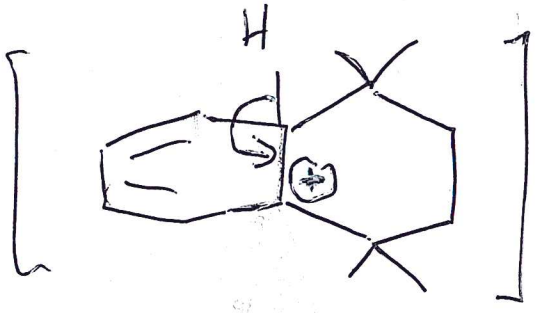
oxonium ion

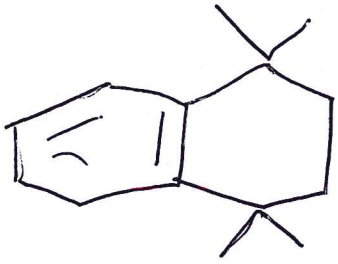
The alcohol reacts with a second proton from the H_2SO_4 to generate an oxonium ion, then another carbocation.



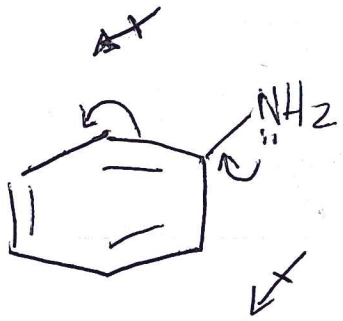
carbocation

This second carbocation then does an intra-molecular Friedel-Crafts reaction to give the provided product.

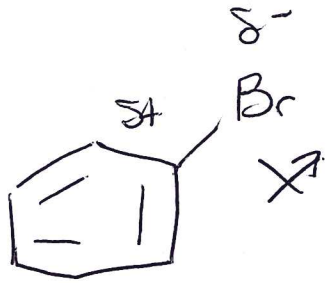




16.71



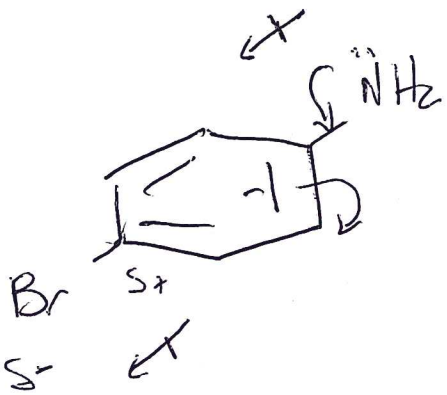
$\mu = 1.53D$



$\mu = 1.52D$

μ is the dipole moment. The larger the dipole moment the greater the polarization of the bond

For the amino group, polarization and the resulting dipole moment is due to its RESONANCE effect The direction (vector) of the dipole moment is <u>towards</u> the benzene ring.



For the bromo group, polarization and the resulting dipole moment is due to its INDUCTIVE effect. The direction of the dipole moment is <u>away</u> from the benzene ring.

16.71 (cont'd)

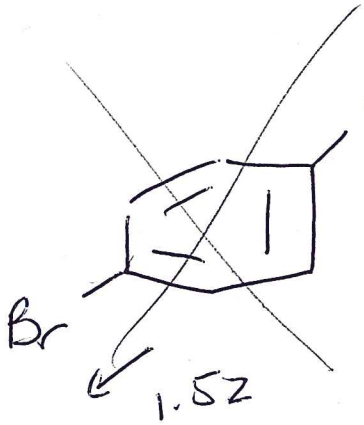
The extent to which the amino group "donates" to the ring, and the extent to which the bromo group "withdraws" from the ring is approximately equal.

μ 1.53D $\cong$ μ 1.52D

AMINO BROMO

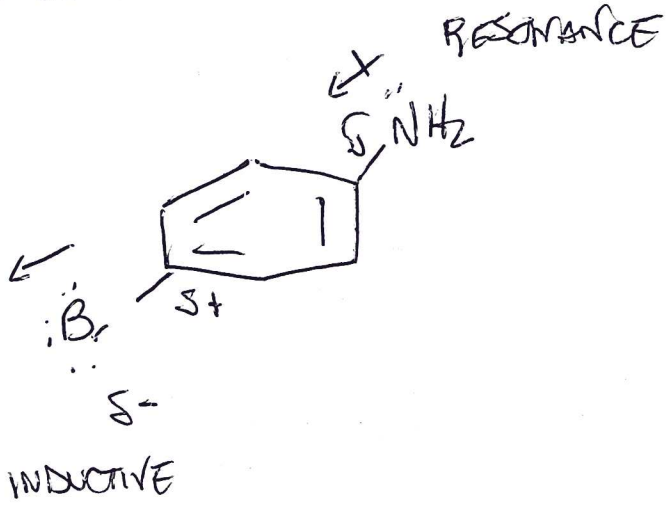
If both the amino and bromo were withdrawing, a para substituted ring would be expected to have a dipole moment of approximately zero, because the two effects would cancel each other out.

But the observed dipole moment is NOT zero. It is 2.91D.



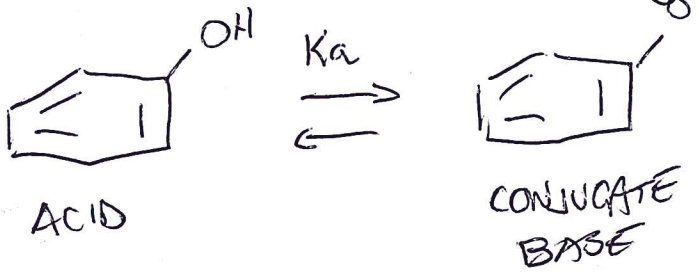
16.71 (cont'd)

The only way to explain the larger dipole moment of 2.91D is if the direction of the polarization is in the same direction



16.73

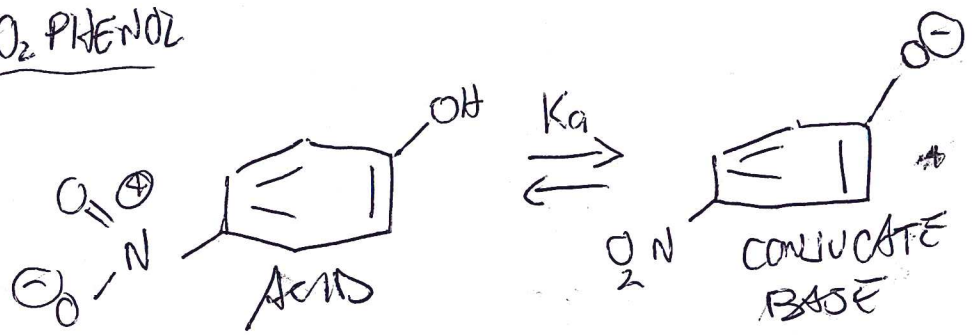
PHENOL



$K_a = \frac{[CB]}{[A]}$

$pK_a = 9.89$

p-NO_2 PHENOL



$K_a' = \frac{[CB]}{[A]}$

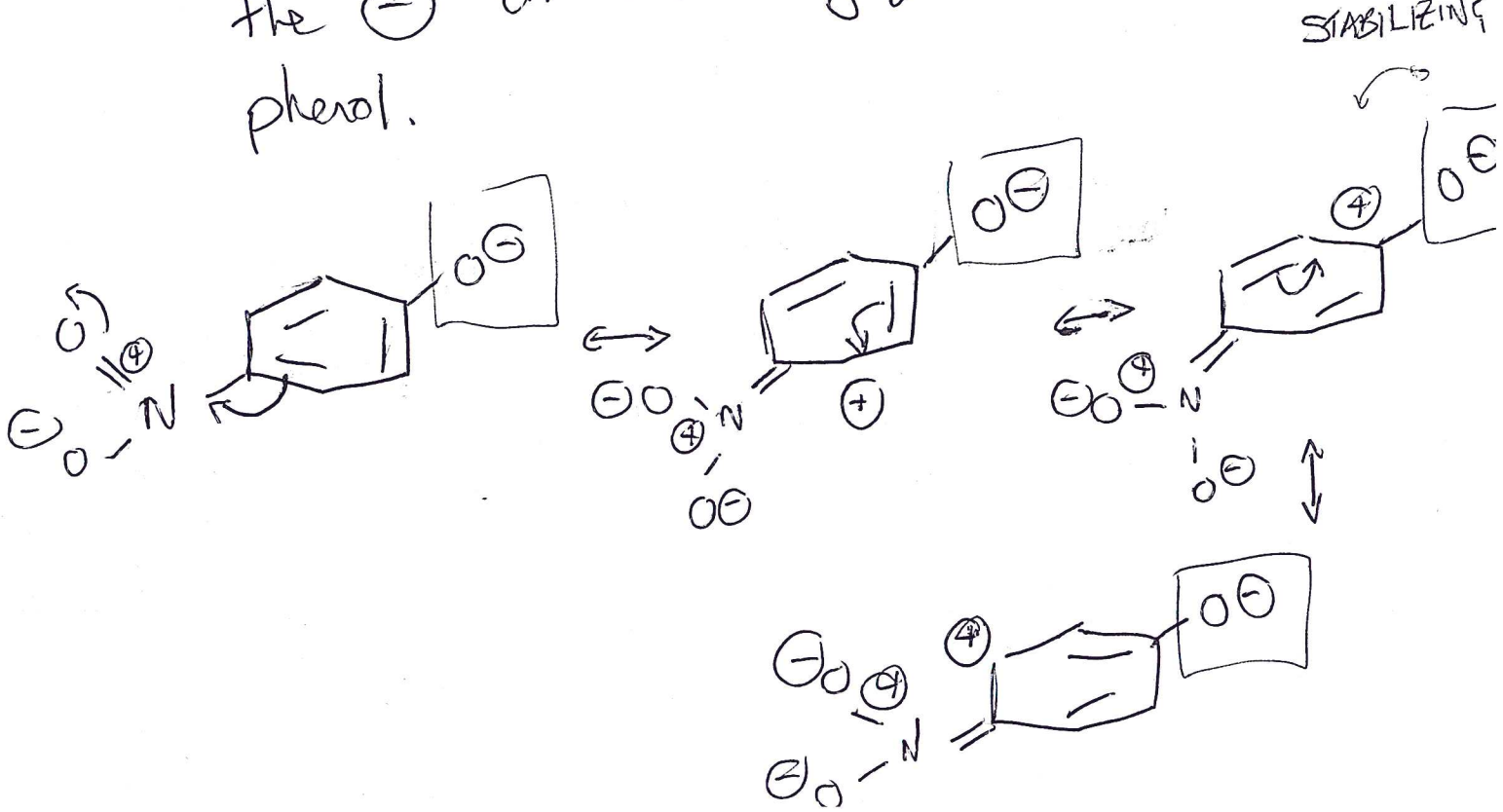
$pK_a = 7.15$

(LOWER than phenol)

16.73 (cont'd)

The lower pKa for p-nitrophenol suggest a higher Ka, a stronger acid and a more stable conjugate base than unsubstituted phenol.

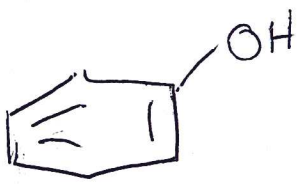
The stability of the conjugate base comes from the electron-withdrawing ability of the nitro group via resonance. The nitro group delocalizes e⊖ out of the ring and makes the ring more ⊕. The ⊕ on the ring stabilizes the ⊖ on the conjugate base of the phenol.



16.73 (cont'd)

The unsubstituted phenol does not have this "extra" stabilizing effect that is present when the nitro group is on the ring.

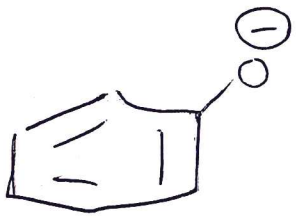
16.74



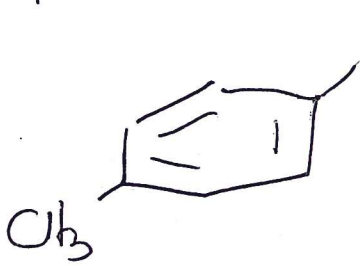
$K_a = \frac{[CB^-]}{[A]}$

PHENOL

K_a ↓↑

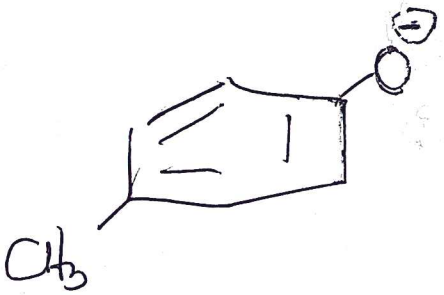


p-METHYL PHENOL



$K_a = \frac{[CB]}{[A]}$

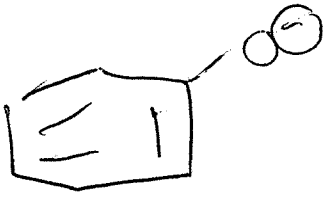
K_a ↓↑



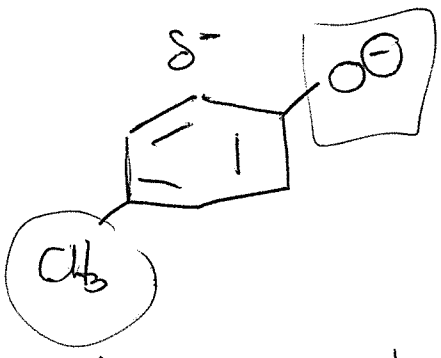
Methyl groups are known to be EDG, even though there is no obvious resonance or inductive effect. This has been determined by experimentation.

16.74 (cont'd)

If the methyl group is ED, it makes the ring more ⊖, relative to the phenol ring



no substituent so ring is "neutral"



EDG makes ring δ-

The more ⊖ ring destabilizes the CB

↓ [CB], ↓ Ka, ↑ pKa

With a methyl group on the ring, it would be expected that methyl phenol has a HIGHER pKa than phenol

17.52

The most acidic (strongest acid, lowest pKa) will have the most stable conjugate base

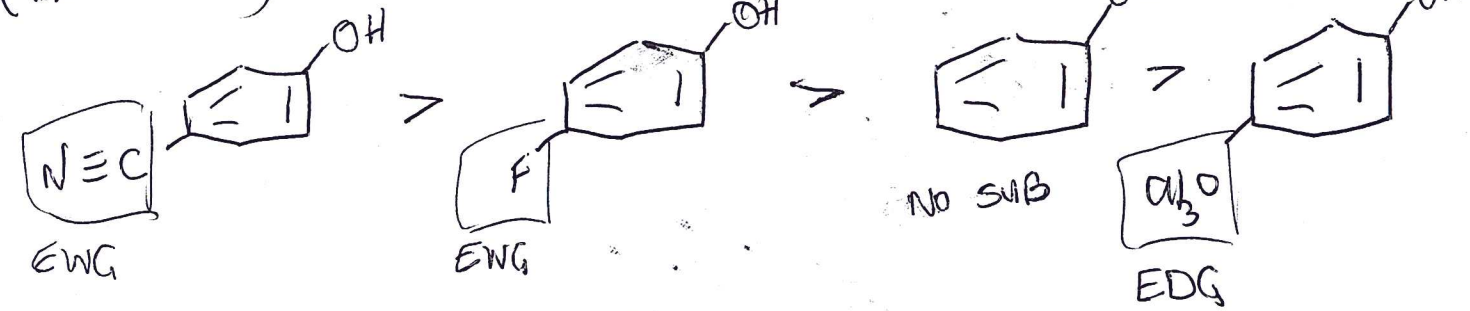
EDG: DESTABILIZE CB ↓ [CB] ↓ Ka ↑ pKa WEAKER ACID

LESS ACIDIC

EWG: STABILIZE CB ↑ [CB] ↑ Ka ↓ pKa STRONGER ACID

MORE ACIDIC

(most acidic)

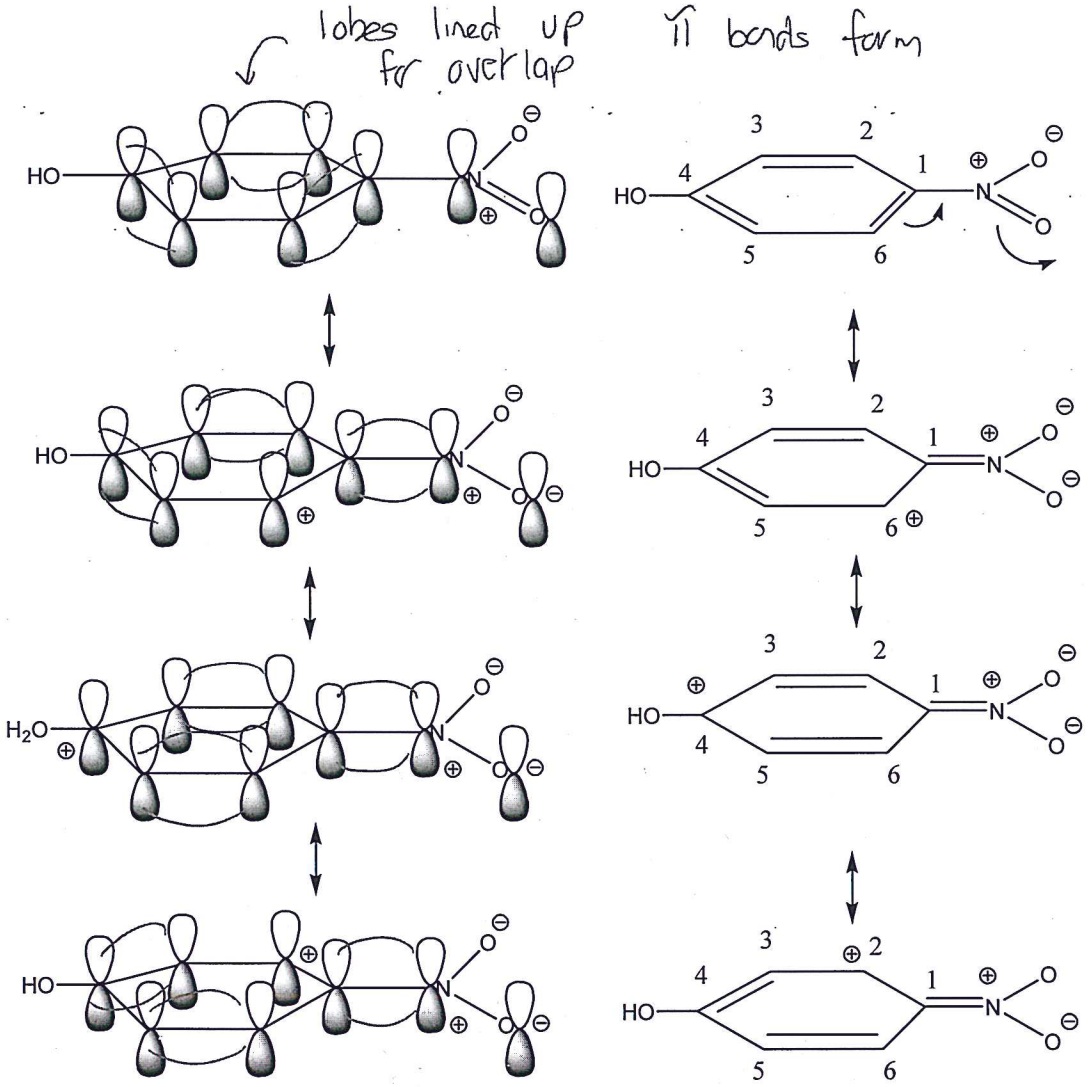


$\sigma_p = 0.66$ > $\sigma_p = 0.06$ > $\sigma = -0.27$ (least acidic)

Use σ para values to determine which substituent is MOST EW

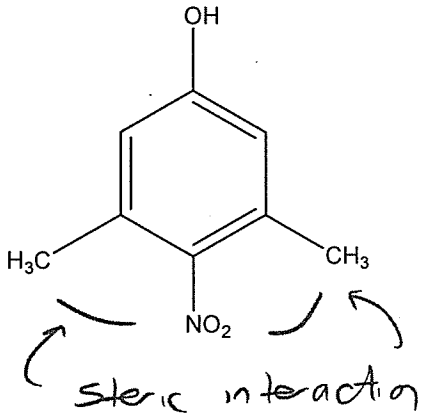
17.57

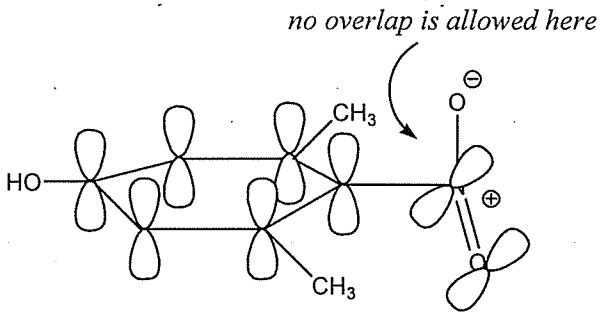
In order for the nitro group to delocalize electrons out of the ring, all of the p-orbitals must be oriented so their lobes can overlap to form p-bonds through which the electrons move. If the lobes of the p-orbitals are out of alignment, then the π bonds cannot form between those atoms and the electrons cannot be delocalized. In p-nitrophenol (and 2,6-dimethyl-4-nitrophenol), the p-orbitals of the nitrogen and oxygen of the nitro group are properly aligned and electrons can flow freely through the π bonds. This allows the electrons to be delocalized out onto the nitro group which makes the ring more positive. The positive ring stabilizes the conjugate base and lowers the pKa relative to unsubstituted phenol.



On the left above are structures that depict resonance structures showing p orbitals. The red curved lines represent overlap of p-orbital lobes resulting in π bonds. The set of structures on the right show the resonance structures using conventional bonding and delocalization of electrons without the p orbitals.

When methyl groups are introduced to the ring at the 3- and the 5-positions of the ring, steric interactions between these methyl groups and the nitro group force the nitro group out of the same plane as the ring. The result is that the p-orbitals of the nitrogen and oxygen atoms of the nitro group are no longer aligned with the p-orbitals of the ring, so electrons cannot be delocalized out onto the nitro group. If the electrons cannot delocalize out onto the ring, the ring does not develop positive character which would stabilize the conjugate base and lower the pKa. The higher pKa for the 3,5-dimethyl-4-nitrophenol suggests this is what is happening. The methyl groups in the 2,6-dimethyl isomer do not affect the nitro group so delocalization occurs, stabilization of the conjugate base occurs and the pKa remains lower.





p-orbitals of the N and O are aligned properly with each other, but not with the p-orbitals of the ring