

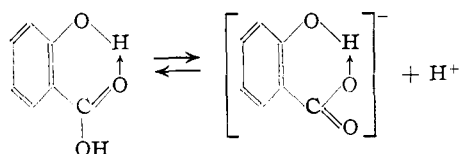
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Relation between Resonance Stabilized Chelate Rings and Acidity

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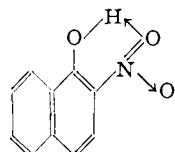
The general effects of chelate rings on the physical properties of organic molecules are well known.¹

It has been shown recently² that the abnormally high acidity of salicylic acid is readily explained by an increased resonance in the anion formed by ionization. Thus



This increased possibility of resonance is brought about by hydrogen bond formation.

It has been assumed³ that the formation of a chelate ring stabilizes the nuclear double bonds in the aromatic ring to which the chelate ring is attached. We have consistent data which seem to prove the corollary of this idea, *i. e.*, that the amount of hydrogen bond formation is greater around a stabilized double bond. The following molecule will serve as an example



Since resonance of the hydrogen atom among the three oxygen atoms of this chelate ring stabilizes the structure, one could expect a higher degree of resonance and consequently greater stability when the steric factors between the hydroxyl and nitro groups are most favorable. This "locking-up" of the ionizable hydrogen should decidedly decrease the acidity of the molecule.

The inductive effect here however is large and is easily transmitted across the double bond.⁴ The decreased acidity predicted above is obvious from the values listed in Table I.

Solvent Effect.—The parallel change in "*pK*" with solvent as shown above indicates that the order of acidity discussed here is not affected by the interaction of solute and solvent.

(1) Lassetire, *Chem. Rev.*, **20**, 259 (1937).

(2) Branch and Yubroff, *THIS JOURNAL*, **56**, 2568 (1934).

(3) Baker and Lothian, *J. Chem. Soc.*, 628-633 (1935).

(4) Fuson, *Chem. Rev.*, **16**, 1-27 (1935).

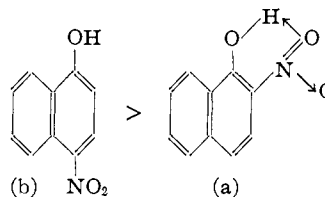
TABLE I
Temperature, 30°

Compound	<i>pK</i>				
	20 cc. (0.05 M) in ethanol				
	+10 cc. (0.05 M) NaOH	+10 cc. H ₂ O	+20 cc. H ₂ O	+30 cc. H ₂ O	+40 cc. H ₂ O
1-Hydroxy-2-naphthonitrile	7.05	6.65	6.40	6.20	6.10
4-Hydroxy-1-naphthonitrile	8.62	8.25	8.00	7.80	7.62
3-Hydroxy-2-naphthonitrile	9.10	8.68	8.40	8.15	8.00
1-Hydroxy-2-naphthaldehyde	8.30	7.90	7.62		
4-Hydroxy-1-naphthaldehyde	8.15	7.70	7.42	7.20	7.05
3-Hydroxy-2-naphthaldehyde	10.20	9.88	9.70		
2-Nitro-1-naphthol	7.35 ^a
4-Nitro-1-naphthol	7.00	6.60	6.32	6.15	6.00
<i>o</i> -Hydroxybenzotrile	8.78	8.35	8.05	7.82	7.68
Salicylaldehyde	9.60	9.20	8.92	8.75	8.65
<i>o</i> -Nitrophenol	8.55	8.15	7.85	7.68	7.58

^a *T* = 35°.

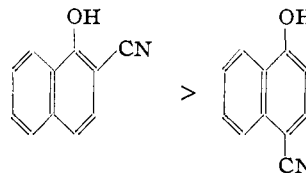
Discussion

It is to be noticed that while the large inductive effect would tend to make (a) more acidic than (b), the reduction caused by chelate ring formation completely overshadows this effect. Thus

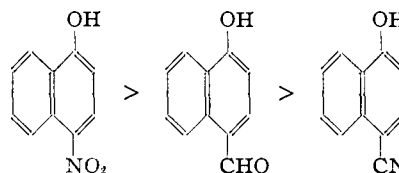


The same situation holds for the corresponding hydroxyaldehydes.

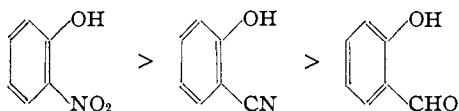
With the cyanonaphthols (no chelate rings) the normal inductive effect becomes important. Thus



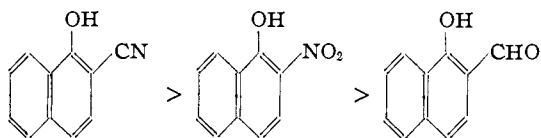
When only the inductive effect is operative the order of acidity is $-\text{NO}_2 > -\text{CHO} > -\text{C}\equiv\text{N}$. Consequently



When some hydrogen bond comes into play this order changes. Thus



When the hydrogen bond becomes very strong a further change takes place as shown.



All of the above observations are explained readily by assuming stronger hydrogen bond formation around a stabilized double bond. The fact that the order of acidity is not the same in the naphthalene and benzene series as shown above clearly proves this point (since all the other factors involved are constant).

We wish to stress that the low acidity of 2-cyano-3-naphthol is in accord with our ideas concerning the structure of naphthalene.⁵

We have shown that the method considered above will locate stabilized double bonds. We will publish soon our work on the Mills-Nixon⁶ problem using the above attack.

Experimental

Apparatus.—The general method was that described in an earlier paper⁵ except that the glass electrode was used throughout.

1-Hydroxy-2-naphthonitrile.—Eleven grams of potassium hydroxide was dissolved in 350 cc. of dried glycerol contained in a three-necked flask equipped with a sealed stirrer. Fifty grams of sodium 1-sulfonate-2-naphthonitrile was added and the stirred solution heated for two hours at 140°. The mixture was poured into a liter of water and acidified with hydrochloric acid. The white precipitate was filtered, dried, and refluxed with 25 cc. of acetic anhydride for thirty minutes. The crude 1-acetoxy-2-naphthonitrile was purified by recrystallization, m. p. 87°; yield 7 g. The hydroxy compound was obtained by hydrolysis with dilute sodium hydroxide. After five recrystallizations from ethanol it melted at 178–179°.

Anal. Calcd. for C₁₁H₇ON: C, 78.09; H, 4.17. Found: C, 78.18; H, 4.25.

4-Acetoxy-1-naphthaldehyde.—Attempts to follow the literature gave disappointing results.⁷ Fifty grams of 4-hydroxy-1-naphthaldehyde was dissolved in a solution of 250 cc. of acetic acid, 50 cc. of acetic anhydride and 20 g. of sodium acetate and refluxed for two hours. The solution was poured into ice water and the precipitate

recrystallized from ethanol; yield 4.5 g., m. p. 103–105°. The material was not quite pure.

4-Hydroxy-1-naphthaldehyde Oxime.—Five grams of 4-acetoxy-1-naphthaldehyde was dissolved in 125 cc. methanol and 60 cc. of water. Three and one-half grams of hydroxylamine hydrochloride, 3.5 g. of sodium acetate and 2.0 g. of sodium bicarbonate were added and the mixture refluxed for fifteen minutes. The methanol was removed until crystallization started. Two hundred cubic centimeters of water was added and the temperature raised to 100°. After cooling slightly, the solution was filtered quickly to remove a resinous portion and crystallization completed in an ice-bath; yield 3 g. (68%), decomposition point 150°.

Anal. Calcd. for C₁₁H₉O₂N: C, 70.57; H, 4.84. Found: C, 71.03; H, 4.95.

The acetyl group is hydrolyzed in the course of the reaction. An attempt to prepare the oxime directly led to unfavorable results.

4-Hydroxy-N-acetoxy-1-naphthaldehyde Oxime.—Thirteen grams of 4-hydroxy-1-naphthaldehyde oxime was dissolved in 100 cc. of glacial acetic acid and 25 cc. of acetic anhydride added. After one hour the precipitate was filtered and washed with dilute acetic acid; yield 14 g. (88%); decomposition point 155°.

Anal. Calcd. for C₁₃H₁₁NO₃: C, 68.11; H, 4.83. Found: C, 67.97; H, 4.86.

4-Hydroxy-1-naphthonitrile.—Fourteen grams of the above compound was heated in 140 cc. of ethanol and 30 cc. of dry pyridine for two hours. The solution was evaporated to one-half volume and poured into dilute hydrochloric acid. The yield of crude nitrile was 9.5 g. (92%); m. p. 173–175°. After recrystallization, m. p. 176–176.5°.

Anal. Calcd. for C₁₁H₇ON: C, 78.09; H, 4.17. Found: C, 77.96; H, 4.21.

This compound also was obtained by the decomposition of the diazonium borofluoride⁸ of 4-cyano-1-aminonaphthalene.

All of the other compounds measured can be produced easily by methods discussed in the literature.

The authors wish to thank the du Pont Company for generous gifts of isomeric aminonaphthalene sulfonic acids.

Summary

1. It has been shown that chelate rings formed around stabilized double bonds are abnormally strong.

2. A method for finding stabilized double bonds has been developed and its limitations completely recognized.

MINNEAPOLIS, MINNESOTA

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(5) Arnold and Sprung, *THIS JOURNAL*, **60**, 1163 (1938).

(6) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

(7) Kamm, McClugage and Landstrom, *THIS JOURNAL*, **39**, 1247 (1917).

(8) Smith and Haller, *THIS JOURNAL*, **61**, 143 (1939).