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EFFECTS OF SUBSTITUENTS ON INTRAMOLECULAR HYDROGEN BONDS OF 2-HYDROXY-4-SUBSTITUTED ACETOPHENONES

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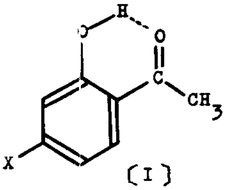
Intramolecular hydrogen bonding in o-substituted phenols has long been studied by many workers.

Recently, Hancock (1) reported the effect of 4- or 5-substituents on both the electronic spectra and acidities of o-nitrophenol.

Nyquist (2) showed out-of-plane deformation of hydroxy group in some intramolecularly hydrogen bonded phenols. Hunsberger and his co-workers (3) discussed the proton chemical shifts of chelated hydrogen in some aromatics and its double-bond character of the bond common to the conjugate chelate and the aromatic ring, and Hay and Williams (4) also reported the proton magnetic resonance of chelated hydrogen. In the previous paper (5) effects of 5-substituents on the intramolecular hydrogen bonds of o-hydroxy acetophenone was studied infrared spectroscopically, and now we wish to report the results with the effects of 4-substituents.



(I)

X: CH_3, CH_3O, H, Cl, Br, NO_2

It was found previously that 5-substituted-2-hydroxyacetophenones showed no absorption bands due to free O-H stretching in the 3600 $cm.^{-1}$ region and that the interacted O-H frequencies (ν^{b}_{OH}) were shifted to longer wave length so far as they merge with the absorptions due to the aromatic C-H stretching vibrations, the resulting broad bands making accurate location of the shifted OH bands difficult. Therefore, intramolecular hydrogen bonds of these compounds were studied with interacted carbonyl stretching modes (ν^{b}_{CO}) (3), (4). Frequencies of the deuterated compounds are shown in Table 1.

TABLE 1

Interacted O-H (ν^{b}_{OH}) and O-D (ν^{b}_{OD}) Stretching Frequencies of 2-Hydroxy-4-substituted Acetophenones.

	Max. absorption ($\nu^{b}_{OH\ max.}$)* ($cm.^{-1}$)	Max. after D.E.** ($cm.^{-1}$)	ν^{b}_{OD} ($cm.^{-1}$)	$\nu^{b}_{OD}/\nu^{b}_{OH\ max.}$ ($cm.^{-1}$)
			2297 ***	1.31
CH_3	3000	2925	2255(S)	1.33
H	3047	2930	2294	1.33
			2280 ***	1.35
NO_2	3080	2930	2277(S)	1.35

* Maximum absorption in 3100-2900 $cm.^{-1}$ region.

** Maximum absorption after deuterium exchange.

*** Shoulder.

As is seen in Table 1, maximum absorption bands in 3080-3000 cm.$^{-1}$ region were shifted to 2930-2925 cm.$^{-1}$ and new bands appeared in the region of 2290-2250 cm.$^{-1}$ by deuterium exchange, the ratio $\nu^{b}_{OD}/\nu^{b}_{OH\ max.}$ being constant.

TABLE 2

Interacted OH Stretching and Out-of-plane Deformation Frequencies (cm.$^{-1}$) of 2-Hydroxy-4-substituted Acetophenones and Measures of Resonance Effect of Each Substituent.

	$\nu^{b}_{OH\ max.}$ in CCl_4 (cm.$^{-1}$)	$\nu^{b}_{OH\ max.}$ in CS_2 (cm.$^{-1}$)	γ_{OH} (cm.$^{-1}$)	γ_{OH} of 2-Hydroxy-5-substituted acetophenones (2)	$(\sigma_p-\sigma')+(\sigma_m-\sigma')$ (6)
CH_3	3012	3000	796.5	783.0	-0.15
CH_3O	2968	2955	818.5	769.0	-0.61
H	3042	3047	788.5	788.5	0
Cl	2974	2970	805.0	778.0	-0.34
Br	3012	3010	802.0	780.0	-0.28
NO_2	3091	3080	784.8	812.0	0.23

Assuming that the hydrogen bonded -OH stretching of these compounds are located in the maximum absorption bands, they were plotted against $(\sigma_p-\sigma')+(\sigma_m-\sigma')$ values (6) which can be taken as a measure of resonance effect of substituents upon the $-COCH_3$ and -OH groups and good linear relationship was established as shown in Fig. 1.

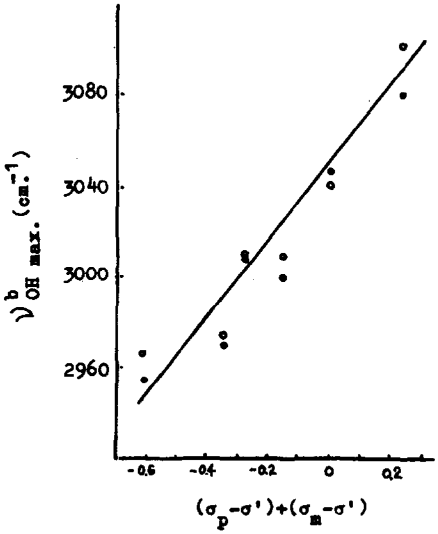


FIG. 1

The Interacted O-H Stretching Frequencies ($\nu^{b}_{OH\ max.}$) in cm.$^{-1}$ as a Function of the Measures of the Resonance Effect ($(\sigma_p-\sigma')+(\sigma_m-\sigma')$) at the Dilute Solution of CCl_4 (○) and CS_2 (●).

The O-H out-of-plane deformation (γ^{b}_{OH}) band which was reported by Nyquist (2) about 2-hydroxy-5-substituted acetophenones, appeared in the region 750-820 cm.$^{-1}$ in this case of the 4-substituted compounds as shown in Table 2.

These frequencies γ^{b}_{OH} were plotted against $(\sigma_p-\sigma')+(\sigma_m-\sigma')$ values to give a good straight line, the sign of the slope being different from that for 2-hydroxy-5-substituted acetophenones as shown in Fig. 2.

On the other hand, the -OH proton chemical shifts of these compounds are seemed to be much influenced by the electrostatic effects of the carbonyl group. Lone pair electrons of the carbonyl oxygen would repel electrons around the OH hydrogen and therefore increase the paramagnetic unshielding.

Electronic effects of substituents would change electron densities both hydroxyl and carbonyloxygen and the differences in pro-

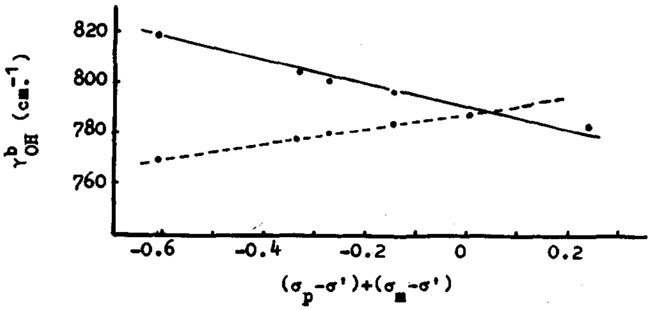


FIG. 2

The Interacted O-H out-of-plane Deformation Frequencies (γ^b_{OH}) of 2-Hydroxy-4-substituted Acetophenones (——) and 2-Hydroxy-5-substituted Acetophenones (------) in cm.$^{-1}$ as a Function of the Measures of the Resonance Effects ($(\sigma_p-\sigma')+(\sigma_m-\sigma')$).

ton chemical shifts might be a function of the kind and position of substituents. The proton chemical shifts measured in CCl_4 solution are shown in Table 3.

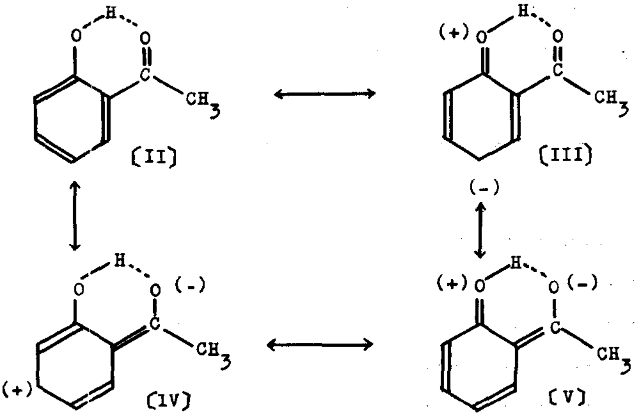
TABLE 3

The Hydroxyl Proton Chemical Shifts, in c.p.s. and p.p.m. Downfield from Tetramethyl Silane, in 2-Hydroxy-4 and 5-Substituted Aceto-Phenones.

	c.p.s.	δ (p.p.m.)
2-Hydroxy-4-methyl-acetophenone	721	12.02
2-Hydroxy-5-methyl-acetophenone	707	11.78
o-Hydroxyacetophenone	723	12.03
2-Hydroxy-4-nitro-acetophenone	729	12.15
2-Hydroxy-5-nitro-acetophenone	765	12.75

The hydroxyl proton resonance signals in these compounds were found more downfield than benzene proton signals at variance with the speculative explanation in our previous paper (5) using equivalent tautomeric mixture. With electron releasing substituents such as methyl, the hydroxyl proton signals are found more downfield when they are in para position than they are meta to the acetyl group. On the contrary, when the substituent is electron withdrawing NO_2 group, the hydroxyl proton signal is found more downfield at the meta position than para.

All these facts may be explained by the reasoning that introduction of an electron withdrawing group in meta to the acetyl group would make the intramolecular hydrogen bond stronger by decreasing electron density on the hydroxyl oxygen together with the enhancement of resonance forms such as structures (III) and (V). When electron releasing groups are at the para position to the acetyl group, hydrogen bond would also be strengthened by the increase in electron density on the carbonyl oxygen and by the increased contribution of structures (IV) and (V).



Enhancement of these resonance structures would elongate the O-H bond, thus causing ν^{b}_{OH} lower, γ^{b}_{OH} higher and proton chemical shift more downfield shift.

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