

# INFLUENCE OF SUBSTITUTION OF AROMATIC NUCLEUS ON FREQUENCY OF VALENCE VIBRATIONS OF GROUPS BONDED BY HYDROGEN BOND

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Received May 10th, 1971

Valence vibration frequencies of amino group of fourteen 4- and 5-substituted 2-nitroanilines in chloroform and acetonitrile and those of O—H bond of fourteen 4- and 5-substituted 2-nitrophenols in tetrachloromethane and fourteen 3- and 4-substituted phenols in acetonitrile have been measured. The influence of the substituents of aromatic nucleus on the valence vibration frequencies of N—H and O—H bonds of the groups bonded by hydrogen bond is discussed.

IR spectroscopy was used for studies of substituent effects in a number of aromatic systems<sup>1,2</sup>. However, the influence of substituents on valence vibration frequencies of systems having their reaction centres bonded by a hydrogen bond has been studied only in a few cases<sup>3-5</sup> so far. This paper deals with a study of substituent influence on valence vibrations of O—H and N—H bonds in hydroxyl and amino groups bonded by an intra- or intermolecular hydrogen bond.

## EXPERIMENTAL

The measurements were carried out using a UR-20 apparatus (Zeiss, Jena) in 1 mm and 0.27 mm cells (solutions in  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$  respectively) at the room temperature. For the measurements of 2-nitrophenols in  $\text{CCl}_4$  1 cm cells were used as in ref.<sup>3</sup> Chloroform and acetonitrile were purified from water and ethanol and checked by their IR spectra in 2 cm cells. The accuracy of readings of absorption maxima was within 0.5–1.5  $\text{cm}^{-1}$  depending on the width of bands.

## RESULTS AND DISCUSSION

Two intensive absorption bands of symmetrical and antisymmetrical valence vibrations of  $\text{NH}_2$  group were found in IR spectra of 2-nitroanilines in the range 3200–3600  $\text{cm}^{-1}$ . Their position depended on the solvent used: in  $\text{CHCl}_3$  these bands of *o*-nitroanilines were in the regions about 3510 and 3400  $\text{cm}^{-1}$ , whereas in  $\text{CH}_3\text{CN}$  they were broader and shifted to lower frequencies due to the intermolecular hydrogen bonds between  $\text{NH}_2$  groups and acetonitrile molecules. The valence vibrations measured are summarized in Tables I–IV.

It is generally known that formation of both the intra- and intermolecular hydrogen bonds between hydrogen atoms of hydroxyl and amino groups and electron donor groups results in lowering the frequency of valence vibrations of the O—H and N—H bonds, and the magnitude of this shift was often used for estimates of strength of the hydrogen bond. Therefore, it can be expected that, similarly to the other properties affected by hydrogen bond<sup>6</sup>, the influence of substituents

TABLE I  
Valence Vibration Frequencies of O—H Bonds in 2-Nitrophenols

Substituent	$\nu(\text{OH}), \text{cm}^{-1}$	Substituent	$\nu(\text{OH}), \text{cm}^{-1}$
4-NH <sub>2</sub>	3 259	4-F	3 259
4-OCH <sub>3</sub>	3 250	4-C <sub>6</sub> H <sub>5</sub>	3 242
4-OH	3 261 <sup>a</sup>	4-Cl	3 248 <sup>a</sup>
4-CH <sub>3</sub>	3 252	4-Br	3 248
4-C(CH <sub>3</sub> ) <sub>3</sub>	3 252	5-Br	3 238
5-CH <sub>3</sub>	3 236	5-NO <sub>2</sub>	3 248
H	3 241	4-NO <sub>2</sub>	3 215

<sup>a</sup> The values taken from ref.<sup>3</sup>.

TABLE II  
Valence Vibration Frequencies of O—H Bonds of Phenols in Acetonitrile Solutions

Substituent	$\nu(\text{OH}), \text{cm}^{-1}$	Substituent	$\nu(\text{OH}), \text{cm}^{-1}$
H	3 409	3,5-(CH <sub>3</sub> ) <sub>2</sub>	3 414
4-NH <sub>2</sub>	3 439	3,4,5-(CH <sub>3</sub> ) <sub>3</sub>	3 426
4-OH	3 422	3-OH	3 402
4-CH <sub>3</sub>	3 415	4-Cl	3 379
3-CH <sub>3</sub>	3 412	3-Cl	3 374
4-OCH <sub>3</sub>	3 420	3-NO <sub>2</sub>	3 346
3,4-(CH <sub>3</sub> ) <sub>2</sub>	3 422	4-NO <sub>2</sub>	3 319

TABLE III  
Valence Vibration Frequencies ( $\text{cm}^{-1}$ ) of N—H Bonds of Anilines in Acetonitrile Solutions

Substituent	$\nu_{\text{asym}}(\text{NH})$	$\nu_{\text{sym}}(\text{NH})$	Substituent	$\nu_{\text{asym}}(\text{NH})$	$\nu_{\text{sym}}(\text{NH})$
4-OH	3 444	3 370	4-Cl	3 468	3 377
4-OCH <sub>3</sub>	3 445	3 370	4-Br	3 464	3 377
3-OCH <sub>3</sub>	3 464	3 378	4-CH <sub>3</sub> CO	3 475	3 380
3-CH <sub>3</sub>	3 459	3 376	4-COOH	3 472	3 379
4-F	3 454	3 373	3-NO <sub>2</sub>	3 469	3 376
3-F	3 466	3 377	4-NO <sub>2</sub>	3 473	3 375

TABLE IV  
Valence Vibration Frequencies of N—H Bonds of 2-Nitroanilines

Substituent	Solutions in chloroform		Solutions in acetonitrile	
	$\nu_{\text{asym}}(\text{NH})$	$\nu_{\text{sym}}(\text{NH})$	$\nu_{\text{asym}}(\text{NH})$	$\nu_{\text{sym}}(\text{NH})$
H	3 518	3 399	3 491	3 369
5-N(CH <sub>3</sub> ) <sub>2</sub>	3 509	3 383	3 486	3 368
5-OCH <sub>3</sub>	3 513	3 389	3 489	3 367
4-OCH <sub>3</sub>	3 514	3 396	3 488	3 369
4-CH <sub>3</sub>	3 516	3 399	3 492	3 371
4-OC <sub>2</sub> H <sub>5</sub>	3 514	3 396	3 491	3 371
5-Cl	3 515	3 396	3 486	3 364
4-F	3 517	3 400	3 490	3 368
4-Cl	3 517	3 399	3 487	3 366
4-Br	3 517	3 398	3 488	3 367
4-I	3 516	3 399	3 488	3 364
5-NO <sub>2</sub>	3 517	3 401	3 485	3 363
4-NO <sub>2</sub>	—	—	3 476	3 350
4-COOH	—	—	3 480	3 359

on the strength of this hydrogen bond must be taken into account in evaluation of the influence of substituents on the valence vibration frequencies. Analogously to the NMR chemical shifts<sup>6-8</sup>,  $pK$  values<sup>6</sup>, and frequencies of the out-of-plane deformation vibrations<sup>6</sup>, the Eqs (1) and (2) should hold for the dependence of valence vibration frequencies of the Hammett substitution constants in the systems containing intra- and intermolecular hydrogen bonds respectively;  $\nu$  and  $\nu_0$  are the valence vibration frequencies of the substituted and unsubstituted compound respectively,  $\sigma_1$

$$\nu = \nu_0 + a\sigma_1 + b\sigma_2, \quad \nu = \nu_0 + a\sigma_1, \quad (1), (2)$$

and  $\sigma_2$  are the Hammett substituent constants ( $\sigma_m$ ,  $\sigma_p$ ) considered with respect to the proton-donor and electron-donor group respectively, and  $a$  and  $b$  are the reaction constants. Similarly to the ref.<sup>6</sup>, the contribution  $c$  (characteristic for the influence of substituents on the strength of hydrogen bond) could again be separated from the constant  $a$ , so that  $a = \rho + c$ , where  $\rho$  stands for all the other effects. The value of this contribution  $c$  cannot be ascertained precisely, it can only be roughly estimated as a difference between the constant  $a$  experimentally found for the system containing a hydrogen bond and that without it. It is possible to foretell its sign. In the case of the valence vibrations frequencies this contribution should be negative — a substituent having  $\sigma_1 > 0$  causes a strengthening of hydrogen bond and hence a change of  $\nu$  towards lower values, on the other hand those with  $\sigma_1 < 0$  weaken the hydrogen bond and cause a shift of  $\nu$  to higher values. Similarly the sign of the constant  $b$  in Eq. (1) can be considered: substituents with  $\sigma_2 > 0$  weaken the intramolecular hydrogen bond causing thus a shift of  $\nu$  towards higher values and *vice versa*, so that the  $b$  constant should be positive. In the systems having the reaction centre bonded to solvent molecules by intermolecular hydrogen bond the constant  $b$  in Eq. (1) loses its meaning<sup>8,9</sup>. The constant  $c$  now characterizes the influence of substituents on the

strength of this intermolecular hydrogen bond and, hence, on the  $\nu$  value, too, and it should be negative as it is the case with the systems having intramolecular hydrogen bonds.

The Eqs (1) and (2) have the following forms for the systems studied ( $R$  and  $r$  are the correlation coefficients of twofold and simple correlation respectively, and  $s$  is standard deviation): 2-Nitrophenols:  $\nu(\text{OH}) = 3242.9 - 40.1\sigma_1^- + 39.1\sigma_2$ ;  $R$  0.926,  $s$  4.5  $\text{cm}^{-1}$ . 2-Nitroanilines in chloroform:  $\nu_{\text{as}}(\text{NH}) = 3514.6 - 1.0\sigma_1 + 5.5\sigma_2$ ;  $R$  0.763,  $s$  1.6  $\text{cm}^{-1}$ ,  $\nu_{\text{sym}}(\text{NH}) = 3394.8 + 0.7\sigma_1 + 11.0\sigma_2$ ;  $R$  0.849,  $s$  2.7  $\text{cm}^{-1}$ . Phenols in acetonitrile:  $\nu(\text{OH}) = 3402.1 - 67.8\sigma^-$ ;  $r$  0.988,  $s$  7.6  $\text{cm}^{-1}$ . 2-Nitroanilines in acetonitrile:  $\nu_{\text{as}}(\text{NH}) = 3488.6 - 8.6\sigma^-$ ;  $r$  0.865,  $s$  2.3  $\text{cm}^{-1}$ ,  $\nu_{\text{sym}}(\text{NH}) = 3367.6 - 12.0\sigma^-$ ;  $r$  0.948,  $s$  0.7  $\text{cm}^{-1}$ . Anilines in acetonitrile:  $\nu_{\text{as}}(\text{NH}) = 3456.7 + 18.5\sigma^-$ ;  $r$  0.880,  $s$  5.1  $\text{cm}^{-1}$ ,  $\nu_{\text{sym}}(\text{NH}) = 3374.4 + 3.9\sigma^-$ ;  $r$  0.610,  $s$  2.7  $\text{cm}^{-1}$ .

In conclusion it can be said that, in accord with the above reasoning about the influence of substituents of aromatic nucleus on the valence vibration frequencies, the constant  $b$  of Eq. (1) is positive in all the cases, and the constant  $a$  of Eqs (1) and (2) is, in all the cases, lower than the values  $d\nu/d\sigma^-$  found for the valence vibration frequencies of  $\text{NH}_2$  and  $\text{OH}$  groups of anilines and phenols measured in inert solvents. In the case of all anilines the contribution of the H-bond term  $c$  to the constant  $a$  is comparable with the contribution  $\rho$ , the result of their reverse parity being a low absolute value of the constant  $a$ , which means that here the correlation of  $\nu(\text{NH})$  vs  $\sigma$  does not exist. A somewhat more favourable situation is encountered with 2-nitrophenols and phenols. The constant  $\rho$  is negative in this case ( $-14.4 \text{ cm}^{-1}$  for solutions of phenols<sup>10</sup> in  $\text{CCl}_4$ ), so that the constant  $a$  should be negative and its absolute value higher than  $\rho$ . This is obviously fulfilled (Eqs for  $\nu(\text{OH})$ ). Also the correlation characteristics confirm here the existence of correlation between  $\nu(\text{OH})$  and  $\sigma$ . The absolute value of the constant  $a$  of the correlation of substituted phenols is 5 $\times$  larger for acetonitrile solutions than that for tetrachloromethane solutions. The magnitude of this constant is interesting not only for its being the highest value of  $d\nu/d\sigma$  found but also for that it makes this IR correlation comparable with the Hammett correlations of other data.

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Translated by J. Panchartek.