

## SOLVENT EFFECT ON VALENCE VIBRATION OF NH BOND OF ACETANILIDES AND PHENYLCARBAMATES

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Wave numbers of IR absorption bands  $\nu(\text{NH})$  of substituted acetanilides and phenylcarbamates were measured in  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_3\text{CN}$  and correlated with the Hammett and Taft substitution constants. Hydrogen bond increases the substituents influence on the wave number of valence vibration of N—H bond.

Solvent induced changes in spectral characteristics are important for evaluation of spectra and for obtaining information about structure of the compound studied. In the case of IR spectra we found<sup>1,2</sup> that magnitude of the polar influence on the valence vibrations of OH and  $\text{NH}_2$  groups depended on formation of intra- and intermolecular hydrogen bonds between these groups and the proton-acceptor groups of the same compound or solvent. A series of simple aromatic compounds was used as a model of influence of hydrogen bond on the substituents polar effects. The polar effect was characterized by empirical substituent constants (the Hammett  $\sigma_{m,p}$  constants) and the influence of hydrogen bond was evaluated by means of the reaction constant  $dv/d\sigma$  of the Hammett equation characterizing the dependence of wave numbers of valence vibration on substituent constants. Thus, in the case of phenols, it was found that absolute value of  $dv/d\sigma$  increased six times when using acetonitrile instead of tetrachloromethane solvent, whereas, in the case of anilines, it decreased.

The purpose of the present paper is to evaluate the influence of hydrogen bond on  $dv/d\sigma$  in the case of NH bond of acetanilides and phenylcarbamates. In the carbamates  $\text{C}_6\text{H}_5\text{NHCOOR}$  used the influence of substituents R on NH bond was only inductive in nature and, therefore, the difference in  $dv/d\sigma$  found in tetrachloromethane solution (free NH bond) and in acetonitrile solution (NH group bonded intramolecularly with the solvent molecules) represents, in fact, the influence of hydrogen bond on only the inductive effects of substituents.

### EXPERIMENTAL

The substituted acetanilides were prepared by acetylation of the respective anilines. The phenylcarbamates were prepared by reaction of phenylisocyanate with the respective alcohols without catalyst. Purity of the compounds prepared was checked by elemental analysis and  $^1\text{H-NMR}$  spectra. IR spectra were measured with the use of a UR-20 spectrometer (Zeiss, Jena) in 1 cm

(CCl<sub>4</sub> solutions), 0.4 cm (CHCl<sub>3</sub> solutions) and 0.027 cm (CH<sub>3</sub>CN) cells. The substituent constants were taken from ref.<sup>3</sup>.

### RESULTS AND DISCUSSION

The valence vibration wave numbers of NH bonds measured in tetrachloromethane, chloroform and acetonitrile solutions are given in Tables I and II (average values from five measurements). These values were correlated with the Hammett ( $\sigma_{m,p}$ ) and Taft ( $\sigma^*$ ) substitution constants in the case of acetanilides and carbamates, respectively; the monoparameter equations obtained (in cm<sup>-1</sup>) are:

$$\nu(\text{N—H}) = 3441.0 - 6.3\sigma; \quad r = 0.889, \quad s = 2.1 \text{ cm}^{-1}, \quad n = 11 \quad (1)$$

$$\nu(\text{N—H}) = 3362.5 - 16.9\sigma; \quad r = 0.992, \quad s = 4.3 \text{ cm}^{-1}, \quad n = 12 \quad (2)$$

$$\nu(\text{N—H}) = 3447.8 - 4.3\sigma^*; \quad r = 0.983, \quad s = 0.87 \text{ cm}^{-1}, \quad n = 10 \quad (3)$$

$$\nu(\text{N—H}) = 3355.0 - 18.8\sigma^*; \quad r = 0.962, \quad s = 1.6 \text{ cm}^{-1}, \quad n = 10, \quad (4)$$

where  $r$ ,  $s$  and  $n$  are correlation coefficient, standard deviation and number of data in a set, respectively. Eqs (1) and (2) refer to the acetanilides in chloroform and acetonitrile, respectively; Eqs (3) and (4) refer to the carbamates in tetrachloromethane and acetonitrile, respectively. The equations indicate that formation of the hydrogen bonds between hydrogen of NH group and acetonitrile molecules has a marked influence on the magnitude of the reaction constant  $d\nu/d\sigma$ . This constant increases almost three times in the case of the acetanilides and four times in the case of the carbamates. This change agrees with what could be expected, as it was the case

TABLE I

Valence Vibration Wave Numbers of N—H Bond of Acetanilides RC<sub>6</sub>H<sub>4</sub>NHCOCH<sub>3</sub> (cm<sup>-1</sup>)

R	$\nu(\text{N—H})$		R	$\nu(\text{N—H})$	
	CHCl <sub>3</sub>	CH <sub>3</sub> CN		CHCl <sub>3</sub>	CH <sub>3</sub> CN
4-NH <sub>2</sub>	—	3 375	4-Cl	3 439	3 358
4-OCH <sub>3</sub>	3 441	3 365	3-F	3 440	3 358
4-CH <sub>3</sub>	3 441	3 365	4-OCCH <sub>3</sub>	3 436	3 355
H	3 439	3 362	4-CN	3 435	3 353
4-F	3 441	3 360	3-NO <sub>2</sub>	3 437	3 351
4-Br	3 439	3 358	4-NO <sub>2</sub>	3 434	3 350

TABLE II  
Valence Vibration Wave Numbers of N—H Bond of Carbamates  $C_6H_5NHCOOR$  ( $cm^{-1}$ )

R	$\nu(N-H)$		R	$\nu(N-H)$	
	$CCl_4$	$CH_3CN$		$CCl_4$	$CH_3CN$
$CH_2:CHCH_2$	3 447.2	3 352	cyclo- $C_6H_{11}$	3 448.5	3 357
$CH_3$	3 447.8	3 355	n- $C_4H_9$	3 448.4	3 356
$C_2H_5$	3 448.2	3 357	i- $C_4H_9$	3 448.4	3 356
n- $C_3H_7$	3 448.4	3 357	s- $C_4H_9$	3 448.7	3 358
i- $C_3H_7$	3 448.7	3 359	t- $C_4H_9$	3 449.1	3 360

with OH and  $NH_2$  groups<sup>1,2</sup>. Electron-acceptor substituents strengthen the intramolecular hydrogen bond between NH group and acetonitrile molecule, which results in a decrease of  $\nu(NH)$ , and, on the contrary, the electron-donor substituents make this hydrogen bond weaker thus shifting the  $\nu(NH)$  towards higher values. As this change in  $dv/d\sigma$  caused by hydrogen bond is negative (the same as  $dv/d\sigma$  in the case of free NH groups), the resulting absolute value of  $dv/d\sigma$  increases. Thus in these cases acetonitrile strengthens the polar influence of substituents on valence vibration of NH bond which is small for the free NH bonds, as it follows from our and other published<sup>4</sup> works.

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