

벤조니트릴에서 니트릴 신축진동과 치환기의 상관관계

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The Correlation of the Nitrile Stretching Frequency with Substituents in Benzonitriles

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Previous investigations on the correlation of infrared stretching frequencies with substituents have dealt almost exclusively with carbonyl stretching frequencies.¹ The present note deals with the effects of substituents on the nitrile stretching frequencies of benzonitriles.

Infrared nitrile stretching frequencies of *p*- or *o*-substituted benzonitriles measured in chloroform, carbon tetrachloride, and potassium bromide are given in Table I. No significant shift was

observed for this infrared nitrile band on changing the solvent from chloroform to carbon tetrachloride. The carbonyl band, on the other hand, was reported to have a shift of approximately 5 cm^{-1} on changing the solvent from chloroform to carbon tetrachloride.¹ This suggests that weak hydrogen bonding does not have a significant influence on shifting the nitrile band in benzonitrile. Kruger, et. al. have observed no noticeable change of the intensity of nitrile stretching frequency in benzonitrile in chloroform and in carbon tetrachloride.² On changing the solvent from chloroform to potassium bromide, however, the nitrile stretching frequencies have shifted $8\text{--}12\text{ cm}^{-1}$ to lower field. *o*-Methyl benzonitrile and benzonitrile have been excluded from this comparison since these two are liquid and are examined neat instead of mixed with potassium bromide.

The values of ν_{CN} have been correlated with two substituent constants, σ , σ^+ , as taken from Ritchie and Sager.³ As can be seen from the correlation coefficients, a better relationship is obtained using σ^+ for all cases in chloroform,

Table I. Nitrile Stretching Frequencies of Benzonitriles (cm^{-1})

Substituent	Solvent		
	CHCl_3	CCl_4	KBr
<i>p</i> -OCH ₃	2216.7	2218.9	2206.0
<i>p</i> -CH ₃	2221.4	2220.9	2209.2
<i>o</i> -CH ₃	2220.9	2221.2	2209.2*
H	2222.5	2224.0	2218.5*
<i>p</i> -Cl	2224.1	2224.4	2216.0
<i>p</i> -NO ₂	2226.7	2226.4	2217.5

a. Measured in the pure liquid state.

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in carbon tetrachloride and in potassium bromide (Table II). In the case of infrared carbonyl stretching frequencies, good correlations of carbonyl stretching frequencies with σ^+ rather than σ have also been reported for acetophenones^{4,5,6} and chalcones.¹ Plots of $\Delta\nu$ against σ^+ for substituted benzonitriles in chloroform, carbon tetrachloride and potassium bromide are shown in Fig. 1, 2, and 3; $\Delta\nu = \nu_X - \nu_H$. The better correlation with σ^+ implies, as explained by Liler⁷ in his study of substituent effects on the carbonyl stretching frequencies, that there is a significant resonance interaction between the

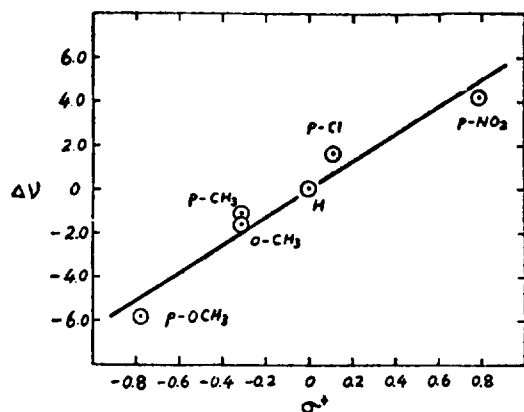


Fig. 1. Plot of $\Delta\nu$ against σ^+ for substituted benzonitriles in CHCl_3 .

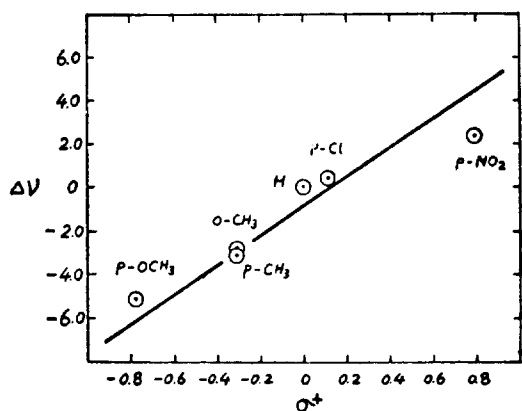


Fig. 2. Plot of $\Delta\nu$ against σ^+ for substituted benzonitriles in CCl_4 .

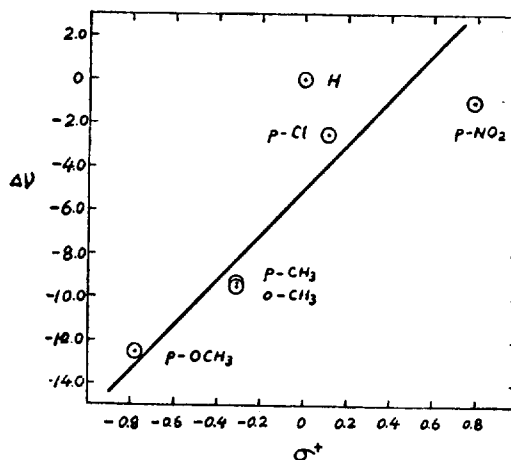


Fig. 3. Plot of $\Delta\nu$ against σ^+ for substituted benzonitriles in KBr.

Table II. Results of Statistical Treatment^a

Solvent	σ^+			σ
	γ	ρ	i	γ
CHCl_3	0.973	9.16	2222.6	0.889
CCl_4	0.968	6.60	2224.9	0.897
KBr ^b	0.838	10.36	2213.4	0.731

a. γ =correlation coefficient; ρ = slope of line, substituent constant vs. ν_{CN} ; i=intercept.

b. *o*-Methyl benzonitrile and benzonitrile were examined neat.

substituent and the nitrile group. The ρ value of 6.19 obtained in chloroform should be compared with the value of 6.24 obtained from a similar study on carbonyl stretching frequencies. It can be seen that there is some scatter in the plot of $\Delta\nu$ vs. σ^+ (Fig. 3) when measured in potassium bromide though we consider both *o*-methyl benzonitrile and benzonitrile are measured in the pure liquid state. Fuson, et. al. also reported a random plot from a study on the correlation of substituents with carbonyl stretching frequencies for acetophenones when recorded in the solid or liquid phase.⁸ Since it has been shown that the Hammett equation is applicable to ortho-substituted series in which the reaction site and ortho substituent are well

separated, correlations of the nitrile stretching frequencies of the ortho-substituted compound were made using the σ^+ value for the para substituent and, as can be seen, a good correlation was obtained.

The infrared stretching frequencies for all the benzonitriles were measured using a JASCO G-13B Spectrophotometer. The spectra were recorded at $27 \pm 3^\circ$. The spectral grades of CHCl_3 and CCl_4 were employed without further purification. All benzonitriles and KBr employed were reagent grade of Aldrich Chemical Co., U. S. A.

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