

벤즈아닐리드에 있어서 치환기가 카르보닐 신축진동에 미치는 영향

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(1973. 1. 18 接受)

On the Correlation of the Carbonyl Stretching Frequency with Substituents in Benzanilides

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(Received Jan. 18, 1973)

요 약. Hammett 형의 식 ($\nu = \nu_0 + \rho\sigma$) 을 적용하여 벤즈아닐리드에 있어서의 카르보닐 신축진동과 치환기의 상관관계를 조사하였다. 치환기가 C-페닐기에 있을 때는 σ 보다 σ^+ 와 더 좋은 상관관계를 나타내었고 한편 치환기가 N-페닐기에 있을 때는 σ 와 더 좋은 상관관계를 나타내었다. 치환기가 C- 및 N- 양페닐기에 동시에 있을 때는 이들 치환기는 카르보닐 신축진동에 서로 독립적으로 작용하였다. 이와같은 결과를 벤즈아닐리드의 구조를 이용하여 고찰하였다.

Abstract. The Correlation of the infrared carbonyl stretching frequency with substituents in benzanilides has been studied. The Hammett-type equation (1) was adopted for this correlation. Substituents in a C-phenyl-ring gave a better correlation with σ^+ rather than σ , meanwhile, substituents in a N-phenyl-ring gave a better correlation with σ . When substituents are placed on both C-phenyl and N-phenyl rings, they influenced the carbonyl stretching frequency reasonably independently of each other.

A conformation of benzanilide which accounts for the above observation has also been discussed.

Introduction

A linear relation of the infrared group frequencies with the Hammett σ (or σ^+) constants in the ring-substituted benzene derivatives has been suggested by several workers.^{1,2,3} Electronic effects of substituents therefore would play an important role in determining the position of the group vibration. The relation is expres-

sed by a Hammett-type equation,

$$\nu = \nu_0 + \rho\sigma \text{ (or } \sigma^+) \quad (1)$$

where ν is the observed group frequency in the ring-substituted compound, ν_0 is the observed group frequency in the unsubstituted derivative, and σ (or σ^+) has its usual significance. Among several groups, the carbonyl group is the one that has been most extensively studied with

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application of the above linear relationship. Some examples of carbonyl stretching frequencies with Hammett substituent constants are acetophenones,⁴ benzoic acids,⁵ ethylbenzoates,² acetanilides,⁶ and chalcones.⁷

This paper presents an additional example of the correlation of carbonyl stretching frequency with the effects of substituents in benzanilides. Substituents are placed either on the *C*-phenyl-ring or on the *N*-phenyl-ring, or on both rings of the benzanilides. The observed effects of electronic transmission of substituents were then discussed considering a molecular conformation.

Experimental

Materials—Benzanilides were prepared from their corresponding ring-substituted benzoic acids and ring-substituted anilines, or from the corresponding ring-substituted benzoyl chlorides and ring-substituted anilines. Identifications of these compounds were made from their melting points (Table 1).

Spectroscopic Measurements—The infrared spectra of benzanilides were recorded on a JASCO G-13 spectrophotometer at $27 \pm 3^\circ$. The spectral grade of chloroform was employed as

Table 1. Benzanilides

Compound No.	Substituents in <i>C</i> -phenyl Rings	Substituents in <i>N</i> -phenyl Rings	mp, °C Observed	mp, °C Lit.	Ref.
1	<i>p</i> -CH ₃ O	H	169	168—169	<i>a</i>
2	<i>p</i> -CH ₃	H	142	140—141	<i>b</i>
3	H	H	161—163	162—163	<i>b</i>
4	<i>p</i> -Cl	H	198	194	<i>c</i>
5	<i>o</i> -Cl	H	114	114	<i>d</i>
6	<i>p</i> -NO ₂	H	211	210—211	<i>e</i>
7	H	<i>p</i> -CH ₃ O	155	156	<i>f</i>
8	H	<i>p</i> -CH ₃	156	157	<i>g</i>
9	H	<i>m</i> -CH ₃	120—123	125	<i>h</i>
10	H	<i>m</i> -CH ₃ O	111		<i>i</i>
11	H	<i>p</i> -Cl	188—192	192—193	<i>j</i>
12	H	<i>o</i> -NO ₂	91—93	94	<i>k</i>
13	H	<i>p</i> -NO ₂	198—199	199	<i>l</i>
14	<i>p</i> -CH ₃	<i>p</i> -CH ₃	160	158—159	<i>m</i>
15	<i>p</i> -Cl	<i>p</i> -CH ₃ O	204		<i>i</i>
16	<i>p</i> -Cl	<i>p</i> -CH ₃	210—211		<i>i</i>
17	<i>p</i> -Cl	<i>m</i> -CH ₃ O	105—106		<i>i</i>
18	<i>p</i> -NO ₂	<i>p</i> -CH ₃ O	194		<i>i</i>
19	<i>p</i> -Cl	<i>p</i> -Cl	202	207—208	<i>n</i>
20	<i>p</i> -NO ₂	<i>p</i> -CH ₃	187	197	<i>o</i>
21	<i>p</i> -Cl	<i>p</i> -NO ₂	217		<i>i</i>
22	<i>p</i> -NO ₂	<i>p</i> -NO ₂	267	266	<i>p</i>

a: Beilstein, "Organische Chemie," 12, 502 (1942), *b*: *ibid.*, 12, 276 (1942), *c*: *ibid.*, 12, 267 (1942), *d*: *ibid.*, 12, 266 (1942), *e*: *ibid.*, 12, 268 (1942), *f*: *ibid.*, 13, 469 (1942), *g*: *ibid.*, 12, 926 (1942), *h*: *ibid.*, 12, 861 (1942), *i*: unknown, *j*: Beilstein, "Organische Chemie," 12, 612 (1942), *k*: *ibid.*, 12, 692 (1942), *l*: *ibid.*, 12, 720 (1942), *m*: *ibid.*, 12, 929 (1942), *n*: *ibid.*, 12, 613 (1942), *o*: *ibid.*, 12, 927 (1942), *p*: *ibid.*, 12, 352 (1942).

Table 2. Carbonyl Stretching Frequencies of Benzanilides

Compound No.	ν , cm^{-1}	$\Delta\nu$
1	1,664.8	-9.0
2	1,669.5	-4.3
3	1,673.8(ν_0)	0.0
4	1,675.5	1.7
5	1,675.5	1.7
6	1,683.5	9.7
7	1,669.0	-4.8
8	1,673.0	-0.8
9	1,674.0	0.2
10	1,674.5	0.7
11	1,677.5	3.7
12	1,687.0	13.2
13	1,686.0	12.2
14	1,666.0	-7.8
15	1,675.7	1.9
16	1,675.5	1.7
17	1,677.5	3.7
18	1,677.5	3.7
19	1,677.0	3.2
20	1,678.0	4.2
21	1,686.2	12.4
22	1,694.0	20.2

solvent.

Results and Discussion

The infrared carbonyl stretching frequencies of substituted benzanilides ($X-C_6H_4-CONH-C_6H_5$), benz-substituted anilides ($C_6H_5-CONH-C_6H_4-Y$), and substituted-benz-substituted anilides ($X-C_6H_4-CONH-C_6H_4-Y$) were summarized in Table 2. The compound number is cited from Table 1. The deviations of the frequencies of ring-substituted derivatives of benzanilide from that of unsubstituted benzanilide ($\Delta\nu = \nu - \nu_0$) are also shown in this table.

The carbonyl stretching frequencies were measured in chloroform rather than in a nonhydrogen-bonding solvent such as carbon tetrachloride because of limited solubility of some of the benzanilides in the latter solvent, and a weak hydrogen bonding did not have a large influence on the transmission of substituent effect.^{7,8} Also the spectra have not been obtained in potassium bromide discs, since in this phase, a poor

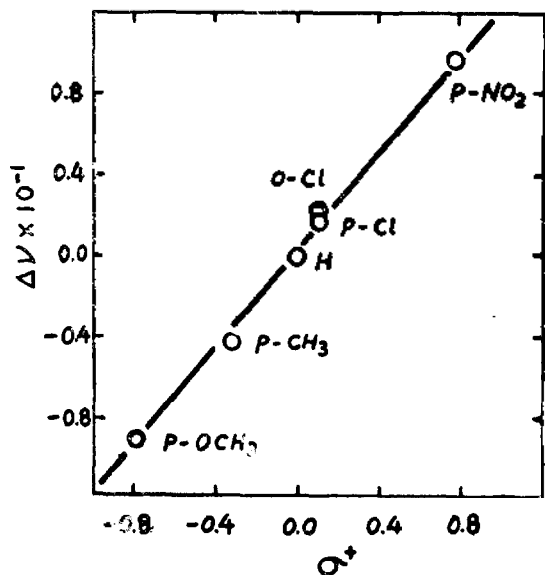


Fig. 1. Plot of $\Delta\nu$ vs. σ^* for benzanilides with substituents in the C-phenyl-ring.

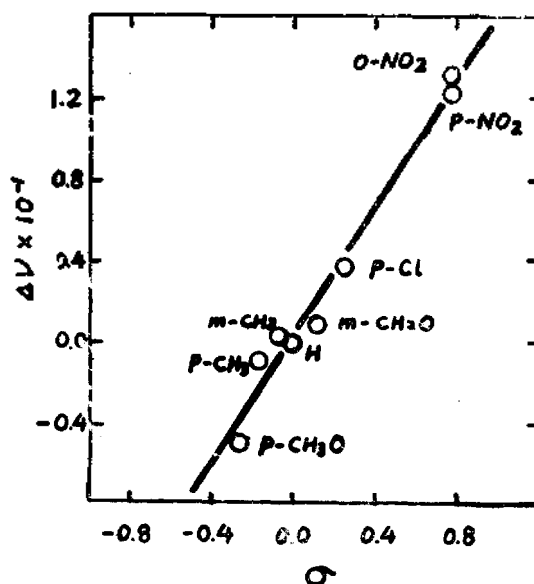


Fig. 2. Plot of $\Delta\nu$ vs. σ for benzanilides with substituents in the N-phenyl-ring.

Table 3. Results of Statistical Treatment

Substituents in	σ				σ^+			
	ρ	γ	i	n	ρ	γ	i	n
C-Phenyl-ring	16.318	0.969	-2.193	6	12.127	0.998	0.110	6
N-Phenyl-ring	15.670	0.988	0.325	8	11.783	0.966	2.187	8

ρ =Slope of the line γ =Correlation coefficient i =Intercept n =Number of point

correlation was observed in the similar study for benzonitriles.⁸

The values of carbonyl stretching frequencies have been examined with two substituent constants, σ , σ^+ as cited from Ritchie and Sager.⁹ Correlations of the carbonyl stretching frequencies of ortho-substituted compounds were made using the σ (or σ^+) values for the para-substituents according to the results of evaluation reported by Baker, et al.¹⁰ and Solomon, et al.,¹¹ and as can be seen in Fig. 1 and 2 the correlations obtained were good. This fact indicates that there is no significant ortho effect of substituents on the carbonyl stretching frequency.

In one series, the substituents are placed on a C-phenyl-ring, in the second on a N-phenyl-ring, and the third series involved placement of substituents on both phenyl-rings. Results of statistical treatment applying the equation (1) are summarized in Table 3. When the substituents are on a C-phenyl-ring, a better correlation is obtained by using σ^+ rather than

σ . This is in agreement with the cases of acetophenone¹² and $RXC=O$ type compounds (where R is an aliphatic or an aromatic radical)¹³. On the contrary, σ constant showed a better correlation with the carbonyl stretching frequency when the substituents are placed on a N-phenyl-ring. The better correlation with σ^+ of the substituent in a C-phenyl-ring implies that there is significant resonance interaction between the substituent and the carbonyl group, since the C-phenyl and the carbonyl groups are coplanar, and the π -bonding orbitals of both groups are all parallel. On the other hand, however, it is not possible to draw a model which shows π -orbitals of N-phenyl and carbonyl groups, and a sp^3 -orbital of intervening amino nitrogen all in parallel (Fig. 3). Hence a little less favorable correlation of σ^+ with the carbonyl group would be observed. However it should be noted that one substituent constant σ^+ (or σ) has only slight advantage over the other substituent constant σ (or σ^+) in correlation with the carbonyl stretching frequency in both cases when the substituents are in a C-phenyl-ring and in a N-phenyl-ring.

As expected, the transmission of electronic nature of the substituent through the N-phenyl-ring was less sensitive than the transmission through the C-phenyl-ring (Table 3). This may be due to the role of intervening amino group.

The lines in Fig. 1 and 2 are expressed as following equations respectively.

$$\nu_{\gamma} = 12.13\sigma^+ + 1,673.91 \quad (2)$$

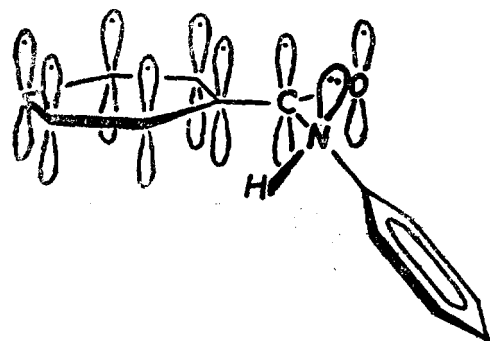


Fig. 3. A schematic representation of π - and sp^3 -orbitals of benzanilide.

$$\nu_X = 15.67\sigma + 1,674.13 \quad (3)$$

Finally, in order to obtain information about the multiple effect of the substituent, substituents were introduced in both phenyl rings of benzanilide, maintaining the substituent in a C-phenyl-ring (X) constant and varying the substituent in a N-phenyl-ring (Y) and vice versa. In a disubstituted benzanilide like X-C₆H₄-CONH-C₆H₄-Y, if a substituent X has the same effect as its effect in X-C₆H₄-CONH-C₆H₅ on the carbonyl group regardless of the substituent Y and vice versa, then a plot of $\Delta\nu_X + \Delta\nu_Y$ (sum of the Δ values of the two monosubstituted benzanilides) against $\Delta\nu_{XY}$ (carbonyl stretching frequency of a disubstituted benzanilide) should give a linear relationship and the slope of the line should be unity. In fact, a good correlation was observed with a line of $\Delta\nu_{XY} = 0.864(\Delta\nu_X + \Delta\nu_Y) - 0.00963$; $\gamma = 0.9459$ for the

plot of $\Delta\nu_X + \Delta\nu_Y$ against $\Delta\nu_{XY}$ (Fig. 4). This suggests that a substituent on a N-phenyl-ring influences the carbonyl stretching frequency in a manner which is reasonably independent of a substituent on a N-phenyl-ring and vice versa. However the substituents placed on both a C-phenyl and a N-phenyl rings do not display their electronic effects to the extent as they do on a C-phenyl-ring or on a N-phenyl-ring independently since the slope of the line (Fig. 4) is smaller than unity.

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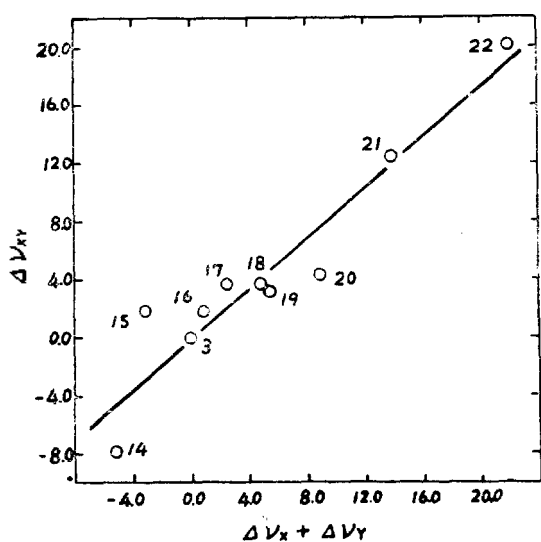


Fig. 4. Plot of $\Delta\nu_X + \Delta\nu_Y$ vs. $\Delta\nu_{XY}$.