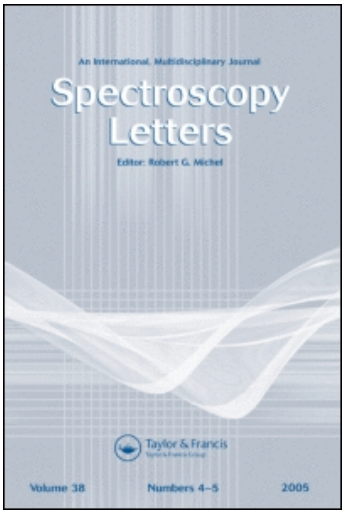

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IR Studies on the Validity of Constants of Ionic Substituents in the Benzylidenemalononitrile Series

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IR STUDIES ON THE VALIDITY OF CONSTANTS OF IONIC SUBSTITUENTS IN THE BENZYLIDENEMALONONITRILE SERIES

KEY WORDS: Infrared spectra; LFER; Ionic substituents; Substituent effect transmission; Benzylidenemalononitriles.

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ABSTRACT

Fourier-transform IR frequencies and integrated intensities of the cyano groups of a series of benzylidenemalononitriles (34 compounds) have been measured in dimethyl sulphoxide. Excellent and satisfactory correlations have been found between spectroscopic features and substituent constants. σ^+ (and other) constants of ionic substituents (three examples) have proved satisfactorily valid in the series studied. The C=C bridge transmits the substituent effects on the intensities twice as strong than the effects of the same substituents on the corresponding frequencies.

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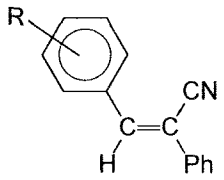
INTRODUCTION

Hammett's equation appears to be applicable to both dipolar (neutral) and unipolar (ionic) substituents [1-4] but the constants of the ionic ones may depend on the geometry, method of measurement employed and solvent [1,5 - 8]. We checked in a previous study [4] σ^+ (and other) constants of one cationic and six anionic substituents; they proved to be satisfactorily reliable to predict the cyano stretching frequencies $\nu(C\equiv N)$ and integrated intensities $A(C\equiv N)$ of *trans*-α-phenyl-β-arylacrylonitriles (Formula **1**) in spite of the essential geometry difference between **1** and the substituted benzonitriles (**2**) in which series those constants were determined quite a long time ago [2].



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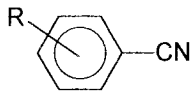

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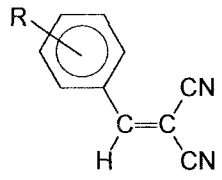

3

Benzylidenemalononitriles (**3**) are a bit more complex model, as they have two different types of cyano groups, so that we hope this series could give some new data on the validity of the constants of ionic substituents, especially about the importance of the influence of the geometry factor on it.

EXPERIMENTAL

Samples of some of the benzylidenemalonitriles studied were available from previous investigation [9]. Others were prepared by Knoevenaglel-type condensations [10] of malononitrile with the corresponding aromatic aldehydes in dry ethanol as a solvent and using

sodium ethoxide as a catalyst. Benzylidenemalononitriles with anionic substituents were prepared by reacting the solutions of the corresponding N-H and O-H acids with equimolar amounts of dry sodium methoxide under argon; their spectra were recorded immediately.

Spectra of 0.1 - 0.2 mol.l^{-1} dimethyl sulphoxide (DMSO) solutions of all the compounds studied were recorded on a Vector 22 Bruker FTIR spectrometer in a CaF_2 cell of 0.13 mm path length at a resolution of 1cm^{-1} and 50 scans. DMSO was chosen for this study, for it dissolves equally well both the neutral compounds and ions studied, and does not react with them.

RESULTS AND DISCUSSION

The frequencies $\nu(C\equiv N)$ and integrated intensities $A(C\equiv N)$ of the cyano stretching bands of the studied series of benzylidenemalononitriles are listed in Table 1. The results of the statistical treatment of the correlations of both $\nu(C\equiv N)$ and the square roots of $A(C\equiv N)$ ($A^{1/2}(C\equiv N)$) with substituent constants (values from Ref. 4) according to the equations of Hammett (1), Brown-Okamoto (2) and Yukawa-Tsuno (3)

$$y = \rho\sigma + b \quad (1)$$

$$y = \rho\sigma^{+} + b \quad (2)$$

$$y = \rho(\sigma^{0} + r^{+}\Delta\sigma_R^{+}) + b \quad (3)$$

are given in Table 2; the graphical comparisons of these values are shown on Figs. 1 and 2. The correlations with Hammett's constants σ are rough ($R=0.91$ for $\nu(C\equiv N)/\sigma$ and $R=0.92$ for $A^{1/2}(C\equiv N)/\sigma$) so they cannot be used for any practical purpose.

As it can be seen in Table 2, both $\nu(C\equiv N)$ and $A^{1/2}(C\equiv N)$ of benzylidenemalononitriles with neutral m- and p-substituents correlate satisfactorily, (according to Jaffe's criteria [1]), with σ^{+} and (σ^{0}, $\Delta\sigma_R^{+}$)

TABLE 1

Infrared data (solvent DMSO) for benzylidenemalononitriles: $R_nC_6H_{5-n}$–CH=C(CN)$_2$.

No.	R	ν(C≡N)[a]	A(C≡N)[b]	No.	R	ν(C≡N)[a]	A(C≡N)[b]
m- *and* p-*substituted compounds*				*Ions*			
1.	H	2228.7	52.8	20.	4 – O^-	2196,91	610.0
2.	4-CH_3	2227.3	71.1	21.	4 – CO_2^-	2227,4	e
3.	4-$(CH_3)_2CH$	2227.2	59.5	22.	4 – CH_3CON^-	2208,7	e
4.	4-C_6H_5	2227.7	80.8				
5.	3,4-$(CH)_4$[c]	2227.4	86.3	o-*Substituted compounds*[f]			
6.	3-HO	2228.3	52.0				
7.	4-HO	2222.9	132.0	23.	2,5-$(CH_3O)_2$	2227.1	58.2
8.	4-CH_3O	2224.5	111.9	24.	2-Cl	2232.2	29.0
9.	3,4-$(CH_3)_2$	2224.2	98.0	25.	2,4-$(Cl)_2$	2232.1	27.8
10.	3-C_2H_5-4-CH_3[d]	2224.3	119.0	26.	2-OCH_3-5-Br	2217.0	122.2
11.	3,4-CH_2O_2	2224.8	99.1	27.	2-NO_2	2235.3	18.1
12.	4-$(CH_3)_2N$	2215.6	261.9	28.	2,4,6-$(CH_3)_3$	2220.7	33.5
13.	4-CH_3CONH	2224.9	94.4	29.	2-thia[g]	2194.1	79.7
14.	4-CH_3S	2225.6	94.8	30.	2-oxa[h]	2213.1	129.3
15.	3-Cl	2230.3	40.0	31.	2,3,5,6-C_8H_8[i]	2227.2	27.5
16.	4-Cl	2229.3	49.7	32.	2,3,4,5-C_8H_8[j]	2230.5	35.5
17.	4-COOH	2230.1	28.2	33.	2,3,4-$C_{10}H_7$[k]	2216.7	103.3
18.	4-CN	2231.1	34.8	34.	2,3-$(CH)_4$[l]	2229.1	40.1
19.	3-NO_2	2231.7	19.2				

[a] In cm^{-1}. [b] In $km.mol^{-1}$. [c] 2-Naphthyl derivative. [d] Methylenedioxy substituent. [e] No reliable data. [f] Not included into the statistical treatment. [g] 2-Thienyl derivative. [h] 2-Furyl derivative. [i] 9-Anthryl derivative. [j] 9-Phenanthryl derivative. [k] Pyrenyl derivative. [l] 1-Naphthyl derivative.

TABLE 2

Correlations of frequencies ν(C≡N) the square roots of intensities $A^{1/2}$(C≡N) ($A^{1/2}$(C≡N) in km. mol^{-1}) of the cyano groups of benzylidenemalononitriles with substituent constants, according to the equations of Brown-Okamoto (Eq.(2)) and Yukawa-Tsuno(Eq.(3)).

No.	Series	Sigma	Slope	b[a]	R[b]	s.d.[c]	n[d]
Correlation of ν(C≡N)							
1.	Neutral compounds	σ^+	ρ=5.96	2228.3	0.9720	0.90	19
2.	Neutral and ions	σ^+	ρ=7.00	2228.6	0.9901	1.16	22
3.	Neutral compounds	$\sigma^0, \Delta\sigma_R^+$	ρ=4.13 r^+=1.86	2228.9	0.9823	0.76	17
4.	Neutral and ions	$\sigma^0, \Delta\sigma_R^+$	ρ=7.18 r^+=0.96	2228.6	0.9913	1.15	20
Correlation of $A^{1/2}$(C≡N)[e]							
5.	Neutral compounds	σ^+	ρ=3.06	5.34	0.9733	0.43	19
2.	Neutral and ions	σ^+	ρ=2.78	5.41	0.9858	0.51	20
3.	Neutral compounds	$\sigma^0, \Delta\sigma_R^+$	ρ=-2.06 r^+=1.88	5.04	0.9805	0.40	17
4.	Neutral and ions	$\sigma^0, \Delta\sigma_R^+$	ρ=-1.95 r^+=1.97	5.01	0.9932	0.37	18

[a] Intercept. [b] Correlation coefficient, 0≤R≤1. [c] Standard deviation. [d] Number of data points. [e] We use in these correlations the square roots of the half-intensities, so the ρ, b and *sd.* values correspond to *one* cyano group.

substituent constants, therefore these correlations can be used for checking the validity of the constants of ionic substituents.

The spectral changes, which accompany the conversion of nitriles into anions are usually essential [2,4,11-15] and this result is in agreement with the strong effects of the anionic substituents on the ν(C≡N) and A(C≡N), reflected by their σ^+ constants [2,4,11]. For example, the

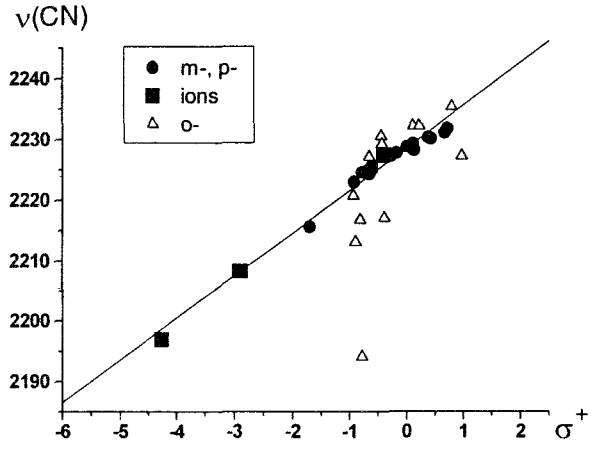

Fig.1 Plot of the ν(C≡N) (cm^{-1}) of benzylidenemalononitriles vs. substituent constants.

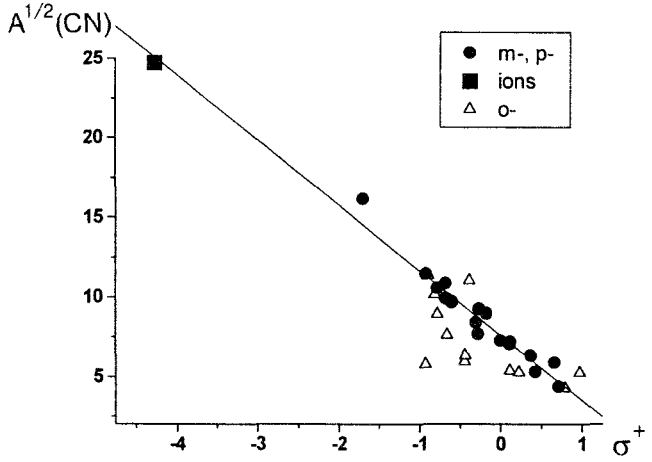

Fig.2 Plot of the $A^{1/2}$(C≡N) (A(C≡N) in km. mol^{-1}) of benzylidenemalononitriles vs. substituent constants.

conversion of 4-hyroxybenzylidenemalononitrile into the anion causes a 26 cm^{-1} decrease in $\nu(C\equiv N)$, a four-fold increase in $A(C\equiv N)$ and a strong intensification of the aromatic skeletal bands near 1600 cm^{-1} and near 1500 cm^{-1} (Fig. 3). The ab inito calculations also give a good description of the spectral changes, taking place in the course of the conversion of 4-hyroxybenzylidenemalononitrile [15] and other nitriles [12-14] into anions and dianions.

Like the case of the substituted *trans*-α-phenyl-β-arylacrylonitriles (Formula **1**) [4], adding the points of ions to the correlations for substituted benzylidenemalononitrile molecules does not deteriorate the correlation factors (Table 2, cf. series 2,4,6 and 8 with series 1,3,5 and 7). Hence, in the series studied, the constants of ionic substituents prove satisfactorily valid and the influence of the geometrical electrostatic factor proves not to be important for their validity.

Ortho-substituted compounds are usually not included in Hammett-type treatments [1]; in certain cases, however, the correlations found are not poor [4]. As it is seen on Figs. 1 and 2, the ortho-substituted benzylidenemalononitriles deviate strongly from the correlation lines. Hence, we can say that the steric hindrance proves to be more essential than the purely electronic ortho effect in the series studied.

The correlation slopes in series 1 and 5 (Table 2), together with literature data [2] for $\nu(C\equiv N)/\sigma^+$ and $A^{1/2}(C\equiv N)/\sigma^+$ slopes in the benzonitrile series (same solvent) make it possible to estimate the transmission coefficient $\pi = \rho(\text{bridged})/\rho(\text{unbridged})$ of the cyanovinylene bridge –CH=C(CN)– (cf. Formulae **2** and **3**). So, using the *frequency* data (series 1) we found the value of 0.66 for this coefficient. This value coincides with π of the phenylvinylene group, calculated on the basis of

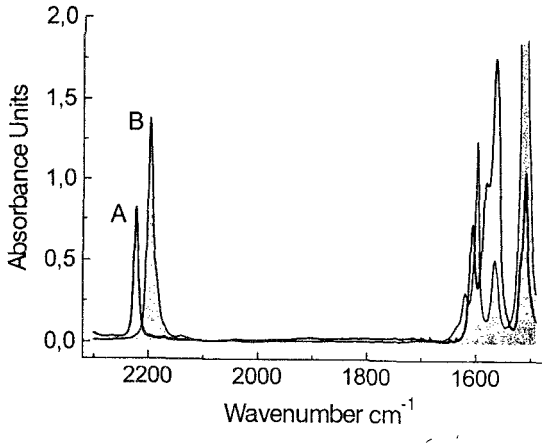

Fig.3 IR spectrum (solvent DMSO) of 4-hydroxybenzyiidenemalononitrile (A) and its anion (B).

ν(C≡N) data (cf. Formulae **2** and **1**) [2]; it lies within the interval of transmission coefficients of 0.45 - 0.85 calculated for various C=C bridges on the basis of both spectroscopic and chemical reactivity data [1,4,9] (and the references therein). However, using the *integrated intensity* data (Table 1, series 5 and those from ref.[2]) gives the twice higher value of 1.30 for π of the cyanovinylene bridge.

CONCLUSION

The joint correlations (for both molecules and ions) found are not worse than those for molecules only, i.e. the constants of ionic substituents prove to be satisfactorily reliable in the series studied. Hence, the geometry factor seems not to be important for the substituent effects themselves, but the same factor plays an important role in their *transmission* through the C=C bridge in the substituted benzylidenemalononitrile molecules and ions.

ACKNOWLEDGEMENT

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