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A LFER study of substituent influence on the FTIR and UV spectral data of 2- and 6-substituted nicotinic acids

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Abstract : The FTIR and UV spectra of the series of 2- and 6-substituted nicotinic acids were determined and the electronic effect of the present substituents and the applied solvents was studied. In order to analyze substituent influence, the FTIR absorption frequencies corresponding to the carbonyl group of the examined compounds were correlated with Hammett equation $\nu = \rho\sigma + h$, where σ is the matching substituent constants for the absorption band of a carbonyl group of the specific compound, and ρ represents the sensitivity of the examined band to substituent effect. Furthermore, UV spectra were recorded in different solvent and again the absorption frequencies corresponding to the carbonyl group were analyzed, this time by Kamlet-Taft equation, in order to quantitatively present solvent influence. The Kamlet-Taft equation is given in the form $\nu_{max} = \nu_0 + s\pi^* + a\alpha + b\beta$ where ν_{max} is the absorption frequency, π^* is a measure of the solvent polarity, α represents the scale of solvent hydrogen bond donor acidities and β represents the scale of solvent hydrogen bond acceptor basicities.

Keywords : Substituted nicotinic acid; UV absorption maxima; FTIR spectra; Hammett equation; Kamelt-taft equation.

INTRODUCTION

Pyridine carboxylic acids have applications in a wide range of fields including industry, pharmacy or biochemistry[1-4] and therefore there is interest in studying the structural and spectrochemical information about them. Seven 2-substituted and 6-substituted nicotinic acids have been synthesized in this study (Figure 1), and their structural properties, from the point of substituent influence, as well as the sol-

X_2 =H; NH_2; Cl; I; CH_3; SH_3; OH; SH

X_6 =H; NH_2; Br; Cl; I; CH_3; OH; SH

Figure 1 : The examined compounds structure

vent effect on them have been examined. The substituent influence was analyzed through FTIR spectra, and the influence of various solvents through UV absorption spectra.

The connection that exists between the compound structure, solvent effect and the absorption spectra has been a subject to many authors[5-12]. One of the reliable and interesting methods to study the electronic effect of present substituents is FTIR spectrometry. The advantage of this method lies in the fact that it displays clearly the functional groups in the molecule and can also detect the change in their electronic structure due to the substituent presence.

The electronic effects of the substituents present in the examined compounds was studied using the Hammett equation[13] (linear free energy relationship – LFER) of the type:

$$\nu_{CO} = \rho\sigma + A \qquad (1)$$

where ν_{CO} is the IR absorption frequency of the C=O group (carbonyl group of the carboxyl –COOH functional group) of the examined compounds, ρ is a reaction constant reflecting the sensitivity of ν_{CO} to the substituent effect, and σ is the substituent constant, the measure of a substituent electronic effect. The analysis of the contribution of the electronic substituent effects shows that these effects have a definite influence on absorption spectra of the investigated acids.

Considering the effect of the UV light on the molecule it hits, one of the possible electronic transition under UV light is the so called n → π* transition - lone electron from the pair in a nonbonding orbital n to higher level antibonding orbital[6]. In the case of investigate compounds (Figure 1), the examined transition was the the n → π* transition in the carboxylic group. The UV spectra were recorded in various solvents and the characteristic absorption maximum wavelengths (λ_{max}) were obtained.

During the excitation process in the n → π* transition the lone electron pair from the carbonyl oxygen is promoted from to an antibonding orbital which contains higher energy. The molecular structure, or the present solvent, can influence the wavelength of the absorption maximum: if λ_{max} increases it is a batochromic shift, while if it decreases it is a hypsochromic shift. Also, batochromic lowers the energy of the electronic n → π* transition, as well as the hypsochromic raises the same energy[6].

The effects of solvent polarity and hydrogen bonding on the absorption spectra of the examined compounds are interpreted by means of the linear solvation energy relationships (LSER) concept, developed by Kamlet and Taft[14], using a general solvatochromic equation (1), of the form:

$$\nu_{max} = \nu_0 + \sigma^* + a\alpha + b\beta \qquad (2)$$

where π^*, α and β are solvatochromic parameters and s, a and b are solvatochromic coefficients, and $\nu_{max} = 1/\lambda_{max}$, the maximum absorption frequency. ν_0 is the reference value, which is taken to be in the solvent cyclohexane, for which all the solvent parameters have the value zero[14].

In Eq. (1), π^* is the index of the solvent dipolarity/polarizability, which is a measure of the ability of a solvent to stabilize a charge or a dipole by its own dielectric effects. The π^* scale was selected to range from 0.00 for cyclohexanone to 1.00 for dimethyl sulfoxide. The α coefficient represents the solvent hydrogen bond donor (HBD) acidity, in other words it describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The α scale extends from 0.00 for non-HBD solvents to about 1.00 for methanol. The β coefficient is a measure of the solvent hydrogen bond acceptor (HBA) bacisity, and describes the ability of a solvent to accept a proton in a solute-to-solvent hydrogen bond. The β scale was selected to extend from 0.00 for non-HBA solvents to about 1.00 for hexamethylphosphoricacid triamide.

EXPERIMENTAL

All applied substituted nicotinic acids acid were commercial product (Fluka – subsidiary of Sigma-Aldrich Corporation, St. Louis, Missouri, USA) of p.a. quality.

Spectroscopic measurements

FTIR spectra were recorded on BOMEM MB-100 spectrometer, using the standard solid specimen technique with KBr.

The UV spectra of the examined compounds were recorded using a Shimadzu 1700A spectrophotometer. The wavelength range was 200-400 nm. The concentrations of the examined solutions were 10-4 mol/dm^3. The solvents used were of high purity, designed for spectroscopic measurements.

RESULTS AND DISCUSSION

2-Substituted nicotinic acids

Hammett equations: analysis of substituent influence

The IR absorption frequencies of the C=O group of the examined 2-substitued nicotinic acids, with the corresponding substituent constants[15] are given in TABLE 1.

The σ_o constant describes the *ortho*- substituent resonance and polar effect:

$$\nu_{CO} = 1663.52 + (38.56 \pm 2.27)\sigma_o$$

R = 0.995, s = 1.92, n = 5

Taft's equation of the dual substituent parameter separates inductive from resonance substituents effect, σ_I and σ_R respectively.

$$\nu_{CO} = 1648.46 + (110.06 \pm 24.21)\ \sigma_I - (82.52 \pm 20.99)\ \sigma_R$$

R = 0.942, s = 6.39, n = 6

The high correlation coefficient values (R>0.90) in both cases confirm that the relationship between the IR absorption frequency and the electronic characteristics of substituent is linear. The substituent effects described by σ_o and σ_I move the examined C=O band to higher frequency values, in other words they raise the energy necessary for the electronic transition in question, while σ_R decreases the absorption frequency, as well as the energy of transition.

Kamlet-Taft equations: solvent – absorption frequency relationship

In this part of the study the solvent – absorption frequency relationship was formed based on the correlation of the absorption frequencies of the C=O group of the examined compounds in different solvents (TABLE 2) with the solvent parameters, by the Kamlet-Taft equation. The Kamlet-Taft parameters are given in TABLE 3.[16]

The calculated correlations of the spectroscopic data with Kamlet-Taft solvent parameters are as follows:

Nicotinic acid

$$\nu_{max} = 54.55 - (17.72 \pm 2.06)\ \pi^* + (3.51 \pm 0.97)\ \alpha - (11.42 \pm 2.09)\ \beta$$

TABLE 1 : IR C=O group absorption frequencies of the 2-substituted nicotinic acids and the corresponding substituent constants

Substituent (X)	$\nu_{C=O}$, cm-1	σ_o	σ_I	σ_R
H	1700	0.00	0.00	0.00
2-NH_2	1703	-*	0.09	-0.48
2-Cl	1713	1.28	0.43	-0.16
2-I	1713	1.34	0.47	-0.12
2-CH_3	1732	0.29	0.01	-0.13
2-SH_3	1683	0.52	0.20	-0.15
2-OH	1713	1.22	0.32	-0.43
2-SH	1683	0.50	0.27	-0.13

TABLE 2 : The UV absorption frequencies of the C=O group of the examined compounds in different solvents

Solvent	ν_{max} * 10^{-3}, cm^{-1}							
	H	2-NH_2	2-SCH_3	2-Cl	2-CH_3	2-I	2-OH	2-SH
Methanol	38.79	40.94	37.49	44.80	37.43	44.89	44.80	33.83
Ethanol	38.89	40.68	37.40	37.17	37.40	37.15	44.88	33.21
Propan-1-ol	38.79	40.58	37.48	37.06	37.60	37.06	44.36	33.33
Propan-2-ol	38.85	40.58	37.45	37.17	37.30	37.17	39.93	30.03
2-methyl-2-propanol	38.89	40.68	37.40	37.17	37.37	37.17	44.82	33.16
Ethylene glycol	36.76	41.12	38.34	37.17	37.29	37.01	44.59	33.38
Butan-1-ol	38.82	40.62	37.23	37.11	37.34	37.11	44.80	33.92
Pentan-1-ol	38.76	40.58	37.26	37.82	37.35	37.88	44.84	32.85
2-methyl-2-butanol	38.83	40.45	37.26	37.95	38.08	37.88	44.60	33.13
Acetonitrile	38.83	40.52	37.54	37.31	37.42	37.55	44.44	33.24
Dimethyl sulfoxide	28.12	29.84	27.30	27.20	27.31	27.22	29.44	25.13
N,N-Dimethylacetamide	37.35	36.87	36.79	36.97	36.94	36.89	36.95	33.18
Tetrahydrofuran	38.86	39.88	37.26	37.04	37.11	37.08	41.32	30.47
Dioxane	38.18	29.89	37.24	37.15	37.40	37.13	35.15	37.15
N,N-Dimethylformamide	29.40	30.15	28.31	30.13	27.24	31.17	30.51	25.34
Ethyl acetate	38.80	37.19	37.42	37.19	37.42	37.24	40.62	33.15

TABLE 3 : Kamlet-taft solvent parameters

Solvent	π^*	α	β
	0.6	**0.93**	**0.62**
Methanol	0.54	0.83	0.77
Ethanol	0.52	0.78	0.83
Propan-1-ol	0.48	0.76	0.95
Propan-2-ol	0.41	0.68	1.01
2-methyl-2-propanol	0.92	0.90	0.52
Ethylene glycol	0.47	0.79	0.88
Butan-1-ol	0.40	0.84	0.86
Pentan-1-ol	0.40	0.28	0.93
2-methyl-2-butanol	0.75	0.19	0.37
Acetonitrile	1.00	0.00	0.75
Dimethyl sulfoxide	0.88	0.00	0.76
N,N-Dimethylacetamide	0.58	0.00	0.55
Tetrahydrofuran	0.55	0.37	0.37
Dioxane	0.88	0.00	0.69
N,N-Dimethylformamide	0.55	0.00	0.45

R=0.956 s=1.22 n=14

2-Aminonicotini acid

$$\nu_{max} = 52.15 - (14.52 \pm 3.16)\,\pi^* + (6.25 \pm 1.48)\,\alpha - (10.25 \pm 3.15)\,\beta$$

R=0.917 s=1.83 n=13

2-(Methylthio)nicotinic acid

$$\nu_{max} = 51.85 - (15.29 \pm 2.57)\,\pi^* + (4.91 \pm 1.20)\,\alpha - (12.06 \pm 2.56)\,\beta$$

R=0.935 s=1.49 n=13

2-Chloronicotinic acid

$$\nu_{max} = 53.34 - (15.61 \pm 3.09)\,\pi^* + (6.21 \pm 1.45)\,\alpha - (14.01 \pm 3.08)\,\beta$$

R=0.925 s=1.79 n=13

2-Methylnicotinic acid

$$\nu_{max} = 51.78 - (15.14 \pm 2.61)\,\pi^* + (5.06 \pm 1.29)\,\alpha - (12.85 \pm 2.66)\,\beta$$

R=0.940 s=1.50 n=13

2-Iodonicotinic acid

$$\nu_{max} = 52.19 - (13.22 \pm 3.07)\,\pi^* + (6.51 \pm 1.51)\,\alpha - (15.06 \pm 3.13)\,\beta$$

R=0.924 s=1.76 n=13

2-Hydroxynicotinic acid

$$\nu_{max} = 59.72 - (17.39 \pm 3.69)\,\pi^* + (9.50 \pm 1.82)\,\alpha - (17.28 \pm 3.76)\,\beta$$

R=0.941 s=2.12 n=13

2-Thionicotinic acid

$$\nu_{max} = 44.89 - (11.39 \pm 2.17)\,\pi^* + (5.30 \pm 1.10)\,\alpha - (12.25 \pm 1.96)\,\beta$$

R=0.947 s=1.27 n=13

In this part of research too, the high correlation coefficient values (R>0.90) in all equations confirms the linear dependence of the UV absorption frequencies on solvent parameters.

Negative values of coefficient for π^* i β, solvent polarity/polarizability and hydrogen bond acceptor ability decrease the absorption frequency values, therefore the energy of the electronic transition too, while the positive coefficient of the parameter α, hydrogen bond donor ability, is directed to the increase of the absorption frequency and the related energy too.

As the coefficient related to π^* has the highest values, in all cases except 2-I and 2-SCH_3 compounds, this effect can be marked as dominant. It points to the decrease of the UV absorption frequencies, as well as to the decrease of the energy of the examined transition.

2-I and 2-SCH_3 compounds have the highest coefficient values for the β parameter, the dominant effect in these two case. It is also directed to the decrease of the examined absorption frequency.

It can be concluded that solvent properties described by π^* i β, which stabilize the excited state, prevail over proton-donor effect (α), which supports the ground state.

6-Substituted nicotinic acids

Hammett equations: analysis of substituent influence:

The IR absorption frequencies of the C=O group of the examined 6-substitued nicotinic acids, with the corresponding substituent constants[15] are given in TABLE 4.

The σ_p constant describes the *para*- substituent resonance and polar effect:

$$\nu_{CO} = 1698.5 - 58.40\sigma_p$$

R = 0.968, s = 3.80, n = 7

Taft's equation of the dual substituent parameter separates inductive from resonance substituent effect, σ_I and σ_R respectively.

$$\nu_{CO} = 1694.7 - (46.57 \pm 15.50)\,\sigma_I - (92.46 \pm 24.55)\,\sigma_R$$

R = 0.902, s = 7.34, n = 7

The high correlation coefficient values (R>0.90) in both cases show that the relationship between the IR absorption frequency and the electronic characteristics of substituent is linear. The substituent effects described by σ_p and σ_I move the examined C=O band to higher frequency values in other words they raise the energy necessary for the electronic transition in question, while σ_R decreases the absorption frequency, as well as the energy of transition.

TABLE 4 : IR C=O group absorption frequencies of the 6-substituted nicotinic acids and the corresponding substituent constants

Substituent (X)	$\nu_{C=O}$, cm-1	σ_P	σ_I	σ_R
H	1700	0.00	0.00	0.00
6-NH_2	1683	-0.66	0.09	-0.48
6-Br	1685	0.23	0.49	-0.16
6-Cl	1683	0.23	0.43	-0.16
6-I	1693	0.18	0.47	-0.12
6-SH	1688	0.15	0.27	-0.13
6-CH_3	1703	-0.17	0.01	-0.13
6-OH	1723	-0.37	0.32	-0.43

TABLE 5 : The UV absorption frequencies of the C=O group of the examined compounds in different solvents

Solvent	ν_{max} * 10^{-3}, cm^{-1}							
	H	6-NH_2	6-Cl	6-CH_3	6-I	6-OH	6-SH	6-Br
Methanol	38.79	37.15	38.02	38.28	38.79	38.97	31.76	37.88
Ethanol	38.89	37.96	37.94	38.42	38.89	38.82	31.11	38.02
Propan-1-ol	38.79	38.31	38.02	38.42	38.79	38.73	31.04	37.88
Propan-2-ol	38.85	37.93	37.91	38.28	38.85	38.67	30.75	38.02
2-methyl-2-propanol	38.89	36.68	38.05	38.48	38.89	38.37	30.71	37.95
Ethylene glycol	36.76	35.17	37.95	35.60	38.76	38.91	31.63	37.82
Butan-1-ol	38.82	37.01	37.95	38.21	38.82	38.67	30.86	37.95
Pentan-1-ol	38.76	38.01	37.95	38.35	38.76	39.61	30.83	37.88
2-methyl-2-butanol	38.83	37.52	37.85	38.35	38.83	38.37	30.47	37.95
Acetonitrile	38.83	37.93	37.95	38.48	38.83	38.67	30.86	38.02
Dimethyl sulfoxide	28.12	27.82	37.09	27.42	38.12	28.28	20.48	37.14
N,N-Dimethylacetamide	37.35	36.78	37.14	36.41	37.35	33.26	30.77	36.36
Tetrahydrofuran	38.86	37.86	38.01	38.40	38.86	38.31	31.74	38.01
Dioxane	38.18	36.83	37.90	38.34	38.18	38.18	37.84	38.01
N,N-Dimethylformamide	29.40	27.46	37.16	27.40	38.40	29.14	21.45	37.35
Ethyl acetate	38.80	38.05	37.94	38.46	38.80	38.49	30.51	37.91

Kamlet-Taft equations: solvent – absorption frequency relationship

The absorption frequencies of the C=O group of the 6-substituted nicotinic acids were also measured (TABLE 5.) and Kamlet-Taft equations were calculated again, using the parameters from TABLE 3.

The results of the correlation of the spectroscopic data with the given Kamlet-Taft solvent parameters are as follows:

6-Aminonicotinic acid:

$$\nu_{max} = 54.58 - (17.98 \pm 2.19) * + (3.95 \pm 1.14) - (12.93 \pm 2.34)\ \beta$$

R=0.955 s=1.30 n=13

6-Cholonicotinic acid:

$$\nu_{max} = 39.04 - (1.22 \pm 0.21)\ \pi^* + (0.45 \pm 0.10)\ \alpha - (0.95 \pm 0.21)\ \beta$$

R=0.945 s=0.12 n=13

6-Methylnicotinic acid:

$$\nu_{max} = 54.02 - (19.14 \pm 2.32)\ \pi^* + (3.63 \pm 1.09)\ \alpha - (10.65 \pm 2.66)\ \beta$$

R=0.957 s=1.37 n=13

6-Iodonicotinic acid:

$$\nu_{max} = 39.75 - (0.99 \pm 0.16)\ \pi^* + (0.25 \pm 0.09)\ \alpha - (0.71 \pm 0.18)\ \beta$$

R=0.924 s=0.10 n=13

6-Hidroxynicotinic acid:

$$\nu_{max} = 53.95 - (15.76 \pm 2.00)\ \pi^* + (5.69 \pm 1.04)\ \alpha - (13.40 \pm 2.13)\ \beta$$

R=0.962 s=1.18 n=13

6-Thionicotinic acid:

$$\nu_{max} = 46.36 - (16.09 \pm 2.49)\ \pi^* + (5.20 \pm 1.17)\ \alpha - (12.98 \pm 2.48)$$

R=0.945 s=1.44 n=13

6-Bromonicotinic acid:

$$\nu_{max} = 39.13 - (1.32 \pm 0.19)\ \pi^* + (0.25 \pm 0.09)\ \alpha - (0.83 \pm 0.19)$$

R=0.936 s=0.11 n=13

The high correlation coefficient values (R>0.90) in all equations confirms the linear dependence of of the UV absorption frequencies on solvent parameters.

Negative values of coefficient for π^* i β, solvent polarity/polarizability and hydrogen bond acceptor ability decrease the absorption frequency values, therefore the energy of the electronic transition too, while the positive coefficient of the parameter α, hydrogen bond donor ability, is directed to the increase of the absorption frequency and the related energy too.

As the coefficient related to π^* has the highest values it can be observed that the solvent polarity/polarizability effect is the prevailing effect in all examined cases.

The conclusion can be derived that applied solvent set stabilizes the excited state to a greater extent than the ground state, for the examined set of 6-substituted nicotinic acids.

CONCLUSIONS

In the case of 2-substituted nicotinic acids, the substituent effect is described by the Hammett equation, containing σ_o and σ_I, *ortho*- and inductive effect, respectively. The substituent effect of the two mentioned properties in the selected compound set is such that it moves the examined C=O band to higher frequency values, in other words the energy necessary for the electronic transition in question increases. On the contrary, the resonant substituent effect, described by σ_R decreases the absorption frequency, as well as the energy of transition.

Considering the solvent effect, it can be noticed that solvent properties described by π^* i β, which stabilize the excited state, prevail over proton-donor effect (α), which supports the ground state.

In the case of 6-substituted nicotinic acids, the substituent effects described by σ_p and σ_I, *para*- and inductive effect respectively, move the examined C=O band to higher frequency values in other words they raise the energy necessary for the electronic transition in question. Contrary to that, equal to the situation with 2-substituted nicotinic acids, the substituent resonance effect presented by σ_R decreases the absorption frequency, as well as the energy of transition.

As for the solvent effect the negative values of coefficient for π^* i β, solvent polarity/polarizability and hydrogen bond acceptor ability decrease the absorption frequency values, therefore the energy of the electronic transition too, while the positive coefficient of the parameter α, hydrogen bond donor ability, is directed to the increase of the absorption frequency and the related energy too, the same as in the case of 2-substituted acids. As the coefficient related to π^* has the highest values, for 6-substituted acids it can be observed that the solvent polarity/polarizability effect is the prevailing effect in for them.

Generally, as the solvent and the substituent effects are in agreement for both compound types, 2- and 6-substituted, the conclusion can be derived that, when nicotinic acids are concerned, the substituent nature is more effective than its position in the molecule structure.

Although a correlation analysis of this type may seem purely theoretical, it can be useful for series of compounds which are a part of a reactivity study, or have practical application as in for example, pharmaceutical industry.

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