Linear free energy approach to the substituent effects in ultraviolet absorption spectra of pyridines. I. Mono- and disubstituted pyridines*

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The substituent effects on the position of the ^1L_a band in the spectra of some monosubstituted and 2,5-disubstituted pyridine derivatives and their benzene analogues as well as the spectroscopic properties of the azaatom are quantitatively discussed in terms of the linear free energy relationships involving new sets of $\sigma_{UV,K}$ spectral substituent constants.

Обсуждено влияние заместителей на сдвиг полосы ^1L_a в спектрах некоторых одно- и 2,5-двухзамещенных производных пиридина и их бензоловых аналогов а также спектральные свойства аза-атома. Обсуждение произведено пользуясь корреляционными уравнениями с новыми спектральными постоянными $\sigma_{УФ,K}$.

Based on the Hammett equation non-equivalent importance has been shown of both the mesomeric and inductive effects operating between the substituent and the reaction site in both the benzene and pyridine systems (see [1] and references quoted therein). It would be interesting to know if a similar variation takes place in the u.v. excitation process within both the mentioned systems. The recently published Hammett type approach to the substituent effects in the ultraviolet absorption spectroscopy of benzene derivatives as presented by eqn (*1*) with so-called spectral $\sigma_{UV,K}$ substituent constants [2—4] gives a possibility of the comparison of the substituent effects on the $\pi \rightarrow \pi^*$ (singlet→singlet) transition in both the pyridine and benzene spectral series in terms of the extrathermodynamic relationship

$$\Delta\nu = \sigma_{UV,K}\, \varrho_{UV,K} + \text{const} \qquad (1)$$

The correlations are carried out separately within the series containing all the substituents of the $+M, I \approx 0$; $-M$, $-I$, and $+M$, $-I$ types respectively, following

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the rules [2—4] of the application of eqn (*1*). All 2-, 3-, and 4-monosubstituted pyridines can formally be considered as *o*-, *m*-, and *p*-substituted benzenes, respectively. Therefore the ^1L_a band shifts (Table 1) in the spectra of the corresponding series have been correlated *vs.* $\sigma_{UV,K,I}$, $\sigma_{UV,K,m}$, and $\sigma_{UV,K,p}$, respectively. The results of the correlations (Table 2) point to another feature of the interactions in the corresponding benzene and pyridine spectral series.

In both 2 (+M) and 4 (+M) pyridine series the mesomeric donation of the +M substituents compensates, to a certain extent, the −M, −I interaction of the azaatom. Hence the $\varrho_{UV,benz}/\varrho_{UV,pyr}$ ratios are below 1 and lower in the case of 4 (+M) substituted pyridine series because also in the excited $\pi \rightarrow \pi^*$ (singlet→singlet) state the mesomeric interactions between the azaatom and 4-substituent are stronger than between the azaatom and the 2-substituents. The same is observed in the equilibrium process (pK_a) [5]. The $\varrho_{UV,benz}/\varrho_{UV,pyr}$ ratios for the series of 2 (−M) and 4 (−M) substituted pyridine series are remarkably over 1 and again higher in the case of 4-substituted pyridine series due to the weak mesomeric azaatom — 4 (−M) substituent interactions [6]. There are weak mesomeric interactions between the substituents and the azaatom in 3-substituted pyridines. The electron donating perturbation of the π-electron system due to the azaatom as given by the $\varrho_{UV,benz}/\varrho_{UV,pyr}$ ratio is almost proportionally relieved by the +M substituent and intensified in the same manner by the −M substituents. Therefore, there are two almost parallel correlation lines followed by such type substituents, respectively.

The azaatom is known as quite a strong −M, −I substituent in kinetic and equilibrium processes [1] but its spectral properties are different. Various exocyclic substituents considered as the formal reaction site in the spectral series (*i.e.* in a similar way as the azaatom here) strongly modify the slopes of the relationship (*1*) [2—4] for monosubstituted benzenes. In contrast to all exocyclic substituents the azaatom only slightly influences these slopes and, therefore, it is a weak spectroscopic substituent. This is due to a weak mesomeric conjugation between the azaatom and the exocyclic substituents and a relatively short distance of the π-electron conjugated system.

Disubstituted pyridines may formally be considered as trisubstituted benzenes, however, the additivity of $\sigma_{UV,K}$ is seriously limited [7] and, therefore, the pyridine ring is considered here as the parent structural unit. The $\tilde{\nu}$—$\sigma_{UV,K,p}$ correlations related to the ^1L_a band shift show that the substituent effects in all of the series of 2,5-disubstituted pyridine derivatives and their benzene analogues are actually regular but not parallel; the $\varrho_{UV,benz}/\varrho_{UV,pyr}$ ratios are almost always above 1 (Table 2).

The spectra of 2,5-disubstituted compounds bearing the formal reaction sites in the position 5 resemble in the position of the ^1L_a band their structural isomers, *i.e.* those with the formal reaction sites in the position 2 and variable substituents in the

Table 1

Positions of the ^1L_a band (in cm^{-1}) in the ultraviolet absorption spectra of monosubstituted pyridines and their benzene analogues (in C_6H_{12})

X	$\tilde{\nu}$, cm^{-1} [a]			
	2-X-Pyridines	3-X-Pyridines	4-X-Pyridines	X-Benzenes [22]
H	51 000 (3.9)	51 000 (3.9)	51 000 (3.9)	50 500
CH_3	49 300 (3.62)	48 500 (3.71)	48 500 (3.52)	48 100
F				48 500
Cl	47 900 (3.77)	47 700 (3.79)		46 500
Br	47 100 (3.82)	46 500 (3.76)		46 300
I				43 500
OCH_3	46 600 (3.78)	46 300 (4.90)	45 700 (3.90)	45 100
SCH_3	40 700 (3.96)	39 600 (4.00)		
NH_2	43 300 (4.00)	43 500 (3.95)	41 100 (4.18)	42 800
$NHCH_3$	40 000 (4.01)			41 100
$N(CH_3)_2$	38 900 (3.99)		38 500 (4.03)	39 800
$NHNH_2$	41 100 (3.98)			41 500
$NHCOCH_3$	43 300 (3.97)	42 600 (3.97)	41 100 (4.23)	41 300
CN	45 300 (4.00)	46 000 (3.99)	45 500 (3.99)	43 400
CHO	43 800 (3.83)	43 500 (3.95)		41 500
$COOCH_3$	45 500 (3.95)	45 800 (3.89)		44 000
$COCH_3$	43 900 (3.81)	44 300 (3.97)	45 200 (4.00)	40 400
NO_2	43 700 (3.84)	41 700 (3.94)	44 500 (3.93)	39 400

a) log ε are given in parentheses.

Table 2

Parameters of the correlation equations in the spectral series of pyridines and their benzene analogues

Spectral series	Series No.	Type of X	$\varrho \times 10^3$ [a]	Intercept $\times 10^3$ cm^{-1}	n [b]	r [c]	$\varrho_{benz}/\varrho_{pyr}$	d
X-Benzenes	1	+M, −M [e]	−14.2	35.4	18	1.000	—	
	2	+M, −M [f]	+76.4	50.5	18	1.000	—	
	3	−M, halogens [g]	+17.5	50.5	12	1.000	—	
	4	+M except halogens [g]	+14.8	50.5	11	1.000	—	
2-X-Pyridines [e]	5	+M	−19.8	31.8	10	0.999	0.72	1 : 5
	6	−M	−10.65	37.3	5	0.995	1.33	1 : 6
3-X-Pyridines [f]	7	+M	+72.6	50.8	7	0.989	1.05	2 : 7
	8	−M	+79.45	52.7	5	0.997	0.96	2 : 8
4-X-Pyridines [g]	9	+M	+21.7	51.3	7	0.994	0.68	4 : 9
	10	−M	+10.5	47.4	3	0.998	1.67	3 : 10
2-X-5-Nitro- and 5-X--2-nitropyridines	11	Halogens	+12.8	38.6	7	0.958	1.10	14 : 11
	12	+M [h]	+24.2	41.8	6	0.998	1.26	15 : 12
	13	+M [i]	+ 8.2	33.0	4	0.985	0.87	16 : 13
p-X-Nitrobenzenes [g]	14	Halogens	+14.1	39.9	5	0.916		
	15	+M [h]	+30.5	43.4	4	0.988		
	16	+M [i]	+ 7.1	30.75	4	0.985		
2-X-5-Phenylazo- and 5-X-2-Phenylazopyridines [g]	17	Halogens	+ 4.4	31.9	8	0.995	0.82	19 : 17
	18	+M except halogens	+ 9.2	33.0	5	0.966	1.11	20 : 18

Table 2 (Continued)

Spectral series	Series No.	Type of X	$\varrho \times 10^{3}$ [a]	Intercept $\times 10^3$ cm^{-1}	n [b]	r [c]	$\frac{\varrho_{benz}}{\varrho_{pyr}}$	d
p-X-Azobenzenes [g]	19	Halogens	+ 3.6	31.6	5	0.982		
	20	+M except halogens	+10.2	32.8	5	0.975		
2-X-5-Acetamido- and 5-X-2-Acetamidopyridines [g]	21	Halogens	+ 4.7	41.85	4	0.977	1.64	23 : 21
	22	+M except halogens	+ 7.8	43.2	7	0.981	1.04	24 : 22
p-X-Acetanilides [g]	23	Halogens	+ 7.7	42.4	5	0.996		
	24	+M except halogens	+ 8.1	43.05	6	0.986		

a) Range of the uncertainty assuming the 90—95% confidence level (the Student test) does not exceed $\pm 0.5 \times 10^3$ in every case, except that for *p*-halogenonitrobenzenes.

b) Number of the experimental points.

c) Correlation coefficient.

d) Numbers of the considered series are also indicated.

e) *Vs.* $\sigma_{UV,K,I}$.

f) *Vs.* $\sigma_{UV,K,m}$.

g) *Vs.* $\sigma_{UV,K,p}$.

h) +M Substituents are H, CH_3, OH, and NH_2.

i) +M Substituents are NH_2, $NHNH_2$, $NHCH_3$, and $N(CH_3)_2$.

Table 3

Characteristics of the ultraviolet absorption spectra of 2,5-disubstituted pyridines

X	$\bar{\nu}$ [cm^{-1}] (log ε)[a]								
	2-X-5-Nitro-pyridines [19, 20]	5-X-2-Nitro-pyridines	*p*-X-Nitro-benzenes [19, 20]	2-X-5-Phenyl-azopyridines [21]	5-X-2-Phenyl-azopyridines	*p*-X-Azo-benzenes [21]	2-X-5-Acet-amidopyridines	5-X-2-Acet-amidopyridines	*p*-X-Acet-anilides
H	41 000 (3.82)	48 500 (3.81) 42 300 (3.70) 37 000 (3.60)	38 600 (3.98)	31 400 (4.28)	45 800 (3.75) 44 400 (3.75) 42 800 (3.40) 31 500 (4.18) 30 000 s (4.02) 29 200 s (3.70)	31 500 (4.34)	40 700 (4.05) 35 700 (3.61) 34 500 s (3.40)	42 600 (4.06) 41 500 (4.07) 41 000 (4.11) 40 100 (4.21) 39 200 (4.17) 38 200 (3.87) 37 000 s (3.49) 35 600 (3.60) 34 800 (3.48)	41 150 (4.02) 36 500 s (2.89) 35 600 (2.74)
CH_3	37 000 (3.79)	49 000 (3.97) 39 800 (3.76) 36 000 (3.81)	36 300 (3.90)	30 900 (4.47)	45 300 s (3.80) 43 700 (3.90) 42 300 s (3.77) 31 700 (4.23) 30 700 (4.28) 29 800 s (4.20) 28 500 s (3.88)	30 800 (4.36)	41 400 (4.02) 35 500 (3.45)	42 500 s (4.00) 41 700 (4.10) 40 900 (4.11) 40 000 (4.10) 39 100 (3.97) 38 100 (3.72) 35 000 (3.60) 33 800 (3.47)	42 800 s (4.00) 41 300 (4.07) 36 100 (2.99) 35 700 s (2.93) 34 800 (2.83)
OH	27 400 (4.00)		31 800 (4.11)	28 800 (5.45)		29 500 (4.39)	40 800 (3.91) 33 500 (3.39)		40 300 (3.86) 34 500 s (3.25)
OCH_3	33 800 (4.01)		32 800 (4.11)	29 600 (4.33)		29 100 (4.44)	40 900 (4.10) 34 100 (3.49)		40 700 (4.09) 34 500 (3.15) 33 300 s (2.92)
SCH_3	29 800 (4.15)		29 600 (4.12)	30 800 (4.42)		27 600 (4.44)	41 100 (4.17) 34 600 (3.58)		41 100 (3.86) 36 800 (4.20)

Table 3 (Continued)

X	$\tilde{\nu}$ [cm^{-1}] (log ε)[a]								
	2-X-5-Nitro-pyridines [19, 20]	5-X-2-Nitro-pyridines	*p*-X-Nitro-benzenes [19, 20]	2-X-5-Phenyl-azopyridines [21]	5-X-2-Phenyl-azopyridines	*p*-X-Azo-benzenes [21]	2-X-5-Acet-amidopyridines	5-X-2-Acet-amidopyridines	*p*-X-Acet-anilides
NH_2	28 600 (4.15)	44 800 (4.21) 31 400s (4.07) 27 900 (4.39)	26 800 (4.23)	28 000 (4.44)		27 500 (4.45)	38 900 (4.10) 32 000 (3.49)	43 000s (2.98) 42 500s (3.28) 41 500s (3.63) 40 900 (3.82) 40 500 (3.82) 39 900 (4.00) 39 000 (4.08) 38 100 (4.00) 37 200s (3.77) 31 300 (3.33)	38 800 (4.05) 33 500s (3.15)
$NHNH_2$	27 600 (4.11)		25 900 (4.20)						
$NHCH_3$	27 500 (4.16)		25 800 (4.27)						
$N(CH_3)_2$	26 900 (4.26)		25 300 (4.30)			25 000 (4.49)			36 900 (4.22) 32 000s (3.34)
F	37 000 (3.79)		38 000 (3.90)	31 500 (4.32)		31 400 (4.36)	41 800 (3.95) 35 600 (3.40)		41 700 (4.22) 35 500 (3.05) 34 500 (2.87)
Cl	35 800 (3.87)	49 000 (3.96) 39 900 (3.84) 35 800 (3.82)	37 200 (4.00)	30 900 (4.37)	43 600 (3.23) 35 000s (3.48) 30 700 (3.91) 29 200s (3.81) 28 300s (3.57)	30 900 (4.45)	40 900 (4.15) 34 900 (3.44)	43 200s (3.54) 42 200s (3.89) 41 600s (4.05) 41 000 (4.19) 40 000 (4.26) 39 000 (4.25) 38 200 (3.93) 37 000 (2.85) 34 200 (3.54) 33 000 (3.32)	40 600 (4.20) 35 400 (2.86) 34 200 (2.61)

Table 3 (Continued)

X	$\bar{\nu}$ [cm^{-1}] (log ε)[a]								
	2-X-5-Nitro-pyridines [19, 20]	5-X-2-Nitro-pyridines	*p*-X-Nitro-benzenes [19, 20]	2-X-5-Phenyl-azopyridines [21]	5-X-2-Phenyl-azopyridines	*p*-X-Azo-benzenes [21]	2-X-5-Acet-amidopyridines	5-X-2-Acet-amidopyridines	*p*-X-Acet-anilides
Br	35 300 (3.95)	49 500 (3.93) 47 600 (3.91) 46 400s(3.88) 38 700 (3.85) 35 500 (3.89)	36 100 (4.00)	30 700 (4.36)	42 900 (3.22) 41 900 (3.22) 41 000 (3.30) 40 000 (3.67) 39 100 (3.83) 38 200 (3.64) 30 700 (4.02) 29 300s (3.91) 28 200s (3.60)	30 700 (4.40)	40 600 (4.16) 34 800 (3.46)	42 500s (3.47) 41 500 (3.69) 41 000 (3.82) 40 100 (3.66) 39 200 (3.69) 38 200 (3.47) 34 400 (3.46) 33 200 (2.97)	40 300 (4.22) 35 500s (2.96) 34 200 (2.77)
I	33 400 (4.07)		34 000 (4.00)	30 200 (4.43)	43 300 (3.84) 35 200s (3.88) 30 200 (4.42) 29 200s (4.35) 27 800s (4.07)	30 200 (4.32)	40 000 (4.27) 34 400 (3.58)	43 200s (3.28) 42 000s (3.32) 41 600s (4.14) 41 000s (4.35) 40 000 (4.48) 39 000 (4.49) 38 100 (4.22) 37 100s (3.32) 33 800 (3.60) 32 800s (3.44)	39 500 (4.30) 36 200s (3.40) 34 600s (3.02) 34 000s (2.82)
$NHCOCH_3$	32 200 (4.19)	46 400 (4.05) 32 200 (4.06)	31 600 (4.05)	29 000 (4.41)		28 900 (4.46)			

a) Wavenumbers involved in the correlations are underlined, s — shoulders and inflections.

position 5 (Table 3). This rule is not fully obeyed in the case of acetamidopyridines perhaps due to an electromerism taking place in the acetamido group [8, 9] and a different influence of the azaatom on it (note a vibrational structure of the ^1L_a band in the spectra of 2-acetamido compounds). It should be mentioned that when the pyridinol-2 $\rightleftarrows$ 1-H-pyridon-2 tautomerism occurs the corresponding points for the 2-OH group deviate, of course, from the correlation.

In conclusion the participation of the azaatom in the conjugated π-electron system in the $\pi \rightarrow \pi^*$ (singlet—singlet) excited state is not too significant and its effectiveness depends mainly on the electronic properties of both the exocyclic substituents and to a much lesser extent on the position of both the latest groups in respect to the azaatom.

Since $\bar{\nu}$—$\sigma_{UV,K}$ correlations are obeyed in the case of title pyridine compounds this correlative approach can safely be applied for diagnostic and predictive purposes in other spectral series of this type, moreover, it stimulates some more qualitative discussions on the substituent effects in the spectra of heterocyclic compounds.

Experimental

Samples of monosubstituted pyridines were either commercially available or prepared according to well known methods and purified as described in original sources. 3-Acetamidopyridine and its derivatives were prepared either according to [10] or as described below. 5-X-Substituted-2-acetamidopyridines *i.e.* those with X = H [11], X = CH_3 [12], X = Cl [13], X = Br [14], X = I [13], and X = NO_2 [15] were prepared and purified as reported in the indicated sources. 5-X-Substituted-2-nitropyridines were prepared and purified according to *Drzeniek* and *Tomasik* [16] and 5-X-substituted--2-phenylazopyridines according to *Tomasik et al.* [17]. The purity of all the investigated samples was additionally tested by the thin-layer chromatography.

The spectra of all monosubstituted pyridines, phenylazopyridines, acetanilides, and acetamidopyridines were measured in cyclohexane solutions (1% of ethyl ether added in the case of acetamido compounds); only the spectra of 2-nitropyridines were recorded in ethanol using a Specord UV VIS (Zeiss, Jena) spectrophotometer. The concentrations of the solutions varied from one sample to another in the range 5×10^{-3}—5×10^{-4} M but in particular cases the concentrations were controlled with a usual precision. Other spectral data concerning 3-nitropyridines, 3-phenylazopyridines, and their benzene analogues are taken from our earlier reports and catalogues [19—22].

All the calculations were performed by least squares method using an Odra-1305 digital computer.

2-Nitro-5-acetamidopyridine

Acetanhydride (2 ml) was added to 5-amino-2-nitropyridine (1 g) [18] and allowed to stand for 6 h. Then methanol (5 ml) was added to hydrolyze the excess of anhydride. The

solid product after evaporation was crystallized from the chloroform—ligroin mixture. Yellow-orange crystalls m.p. 167—169°C were obtained.

For $C_7H_7N_3O_3$ (181) calculated: 46.41% C, 3.87% H, 23.20% N; found: 46.52% C, 3.85% H, 23.28% N.

2-Amino-5-acetamidopyridine

2-Nitro-5-acetamidopyridine (1 g) was catalytically reduced following the procedure recently described [10]. The crude product was crystallized from methanol. Yellowish crystalls m.p. 182.5—183.5°C were obtained.

For $C_7H_9N_3O$ (151) calculated: 55.63% C, 5.69% H, 27.81% N; found: 55.74% C, 6.06% H, 27.84% N.

2-Acetamido-5-aminopyridine

2-Acetamido-5-nitropyridine (5.4 g) [15] was reduced by means of iron powder in acetic acid following the procedure recently described [10]. Colourless crystalls were obtained after crystallization from water; m.p. 153°C.

For $C_7H_9N_3O$ (151) calculated: 55.63% C, 5.69% H, 27.81% N; found: 55.73% C, 5.84% H, 27.40% N.

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