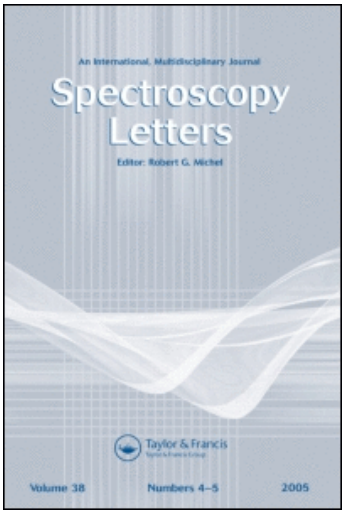

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Danuta Rasała[a]; Waldemar Iwanek[a]; Stanisław Styrcz[a]
[a] Institute of Chemistry, Pedagogical University, Kielce, POLAND

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SUBSTITUENT EFFECTS ON ELECTRONIC SPECTRA OF VICINALLY SUBSTITUTED 2-, 3- AND 4-AMINOPYRIDINES

KEY WORDS: Aminopyridines, Electronic spectra, Substituent effect, CNDO/S

Danuta Rasała,* Waldemar Iwanek and Stanisław Styrcz
Institute of Chemistry, Pedagogical University, Pl-25-020 Kielce
POLAND

ABSTRACT

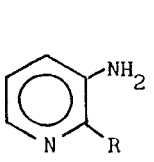
The electronic spectra of forty vicinally substituted 2-, 3- and 4-aminopyridines have been discussed. The low-energy transition of 17 derivatives was analyzed with the help of CNDO/S calculations. In general, the experimental band corresponds to two theoretical transitions. The dual substituent parameter approach (DSP) quite well explains the frequency of one transition in the long-wavelength region of the experimental spectrum.

INTRODUCTION

Much work has been done on correlations of substituent constants with UV absorption frequencies and, to a lesser extent with intensities.[1] There are a number of difficulties inherent in such studies. In practice, the position of overall band maximum is usually used in correlation analyses particularly in the case of aro-

matic compounds. The literature studies can be subdivided into ones where the substituent is (i) directly attached to an aromatic chromophore or (ii) attached to an aromatic system not conjugated to the actual chromophore of interest. It should be mentioned that most substituted aromatic compounds represent a class of derivatives where the orbitals of substituents are directly involved in the UV transitions, and thus, good results should not be expected.[1] On the other hand, most correlations contain an inadequate set of substituents. Moreover, the different relationships with regard to donors and acceptors are discussed. More reasonable results were found if the substituent being varied is not a part of the chromophore measured.[2] There are some reports[2,3] which indicate that interactions between the substituent and the benzene π-electron system need not necessarily be weak. Literature data do not involve studies on vicinally substituted (hetero)aromatic systems.

Recently, the substituent effect on the reactivity[4] as well as on ^{1}H and ^{13}C NMR spectra[5] of comprehensive series of vicinally substituted 2-, 3- and 4-aminopyridines has been widely discussed. In order to obtain information on such derivatives, also in the exited state,[6] the substituent effect on electronic spectra of 2-substituted (Series **1**) and 4-substituted 3-aminopyridines (Series **2**), 3-substituted 2-amino- (Series **3**) and 4-aminopyridines (Series **4**) is discussed in the present work.



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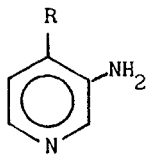

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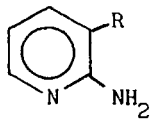

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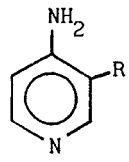

4

Previously the electronic spectra of some aminopyridines were investigated from different points of view.[7-11]

EXPERIMENTAL

Syntheses and purifications of aminopyridines studied in this paper have been described before.[4]

UV-VIS absorption spectra were recorded on a SPECORD M 40 spectrophotometer at 20.0±0.1°C. The solutions in 95% ethanol[12] in the concentration range 10^{-5}M were measured in the 1 cm quartz cell.

Calculations were carried out by the CNDO/S method following Del Bene and Jaffé.[13] The geometry was optimized using the AM1 procedure.[14] The Gaussian analysis[15] was performed on the long-wavelength band. The number of bands used as an entry in the Gaussian analysis was that obtained for 17 compounds from CNDO/S method.[16]

The spectral parameters of the long-wavelength band observed directly in the spectrum and found by the Gaussian analysis are summarized in Tables 1 - 4.

RESULTS AND DISCUSSION

In general, the electronic spectra of compounds under study show two absorption regions. However, when the electron-withdrawing group such as NO_2, CO_2Et, $CONH_2$ and CN is present, the third band is observed. There are some other exceptions among the spectra of Series 2 and 4 (see Table 2 and 4). Thus, the low-intensity shoulder appears on the short-wave side of the high-intensity main band in the spectra of Series 2 (R = NH_2, NHMe and NMe_2) as well as of Series 4 (R = NHMe and NMe_2). For other compounds of Series 4 the shoulder is observed on the long-wave side of the main band. The low-intensity long-wavelength band is the most asymmetrical. It indicates the contribution of variable nature transitions. The shorter-wavelength high-intensity band observed in the region 41000--39500 cm^{-1}, except for the nitro group, is almost insensitive to the substituent effects and is not discussed here.

As seen the ring position of both the exocyclic substituents as well as their electronic properties influence the spectra of the compounds studied. A red shift is relatively large for the long-wa-

TABLE 1

Spectral Parameters[a] of 2-Substituted 3-Aminopyridines (Series 1)

R	Observed		Found (Gaussian Analysis)					
			Band I			Band II		
	$10^3\nu$	logε	$10^3\nu$	logε	10^{-2}f	$10^3\nu$	logε	10^{-2}f
H	33.10	3.57	34.71	3.41	1.63	32.64	3.36	1.03
Me	33.55	3.74	35.07	3.50	3.73	33.09	3.60	2.60
Cl	32.75	3.77	34.41	3.50	4.90	32.48	3.65	3.20
Br	32.55	3.78	34.13	3.54	4.76	32.25	3.64	3.00
OMe	33.89	3.83	35.71	3.49	3.28	33.65	3.72	5.19
CO_2Et	29.09	3.84	32.18	3.24	1.05	28.63	3.83	7.60
$CONH_2$	29.21	3.80	32.37	3.44	1.69	29.20	3.76	5.20
CN	29.29	3.78	31.23	3.44	1.51	28.98	3.74	5.16
NO_2	25.46	3.77	27.63	3.55	1.12	25.42	3.67	2.25
NH_2	34.20	3.84	34.34	3.52	2.07	31.13	3.62	4.33
NHMe	32.28	3.83	34.11	3.50	2.51	31.97	3.74	4.28
NMe_2	32.39	3.81	34.22	3.49	2.24	32.11	3.70	4.31

[a] ν is the wavenumber (cm^{-1}) in the maximum of the band, logε is the molar extinction coefficient in the maximum ($M^{-1}cm^{-1}$), f means the oscillator strength.

velength band of all Series when the electron-withdrawing group is present. A blue shift is observed for compounds of Series **4** in comparison with those of other Series. It corresponds to the most basic aminopyridines studied.[4] Therefore, it could be concluded that the *n* orbital localization on the ring aza atom is a determinant factor of the blue shift.[17] However, in Series **4** the substituent causes the strongest red shift of the band position considered in relation to that of the parent compound as 4-aminopyridine is. Similarly, when NHX (X = H, Me) and NMe_2 groups occupy the position 4

TABLE 2

Spectral Parameters[a] of 4-Substituted 3-Aminopyridines (Series 2)

R	Observed		Found (Gaussian Analysis)					
			Band I			Band II		
	$10^3\nu$	logε	$10^3\nu$	logε	10^{-2}f	$10^3\nu$	logε	10^{-2}f
H			see Table 1					
Me	33.90	3.77				33.78	3.46	1.58
OMe	34.98	3.63				34.82	3.62	0.81
CO_2Et	28.09	3.69	30.27	3.41	1.45	27.85	3.58	2.82
NO_2	24.60	3.81	26.31	3.54	1.41	24.10	3.68	3.11
NH_2[b]	34.29	3.71	39.27	3.26	0.26	33.87	3.63	1.25
	39.20	3.48						
NHMe[b]	34.15	3.79	38.29	3.56	1.47	33.95	3.70	4.27
	38.13	3.56						
NMe_2[b]	33.40	3.90	38.09	3.60	2.39	33.11	3.88	12.90
	38.02	3.71						

[a]See Table 1; [b]The short-wavelength band is the shoulder.

(Series 2). This means a more effective interaction between the nonbonding electron pair(s) of the (hetero)atom attached to the ring and the pyridine π-electron system. In this case the *p* orbital of the nonbonding electron pair is parallel to the π orbital of the ring.[18] According to our earlier NMR studies[5], the bathochromic shift is attributed to an increase of the conjugation of the substituent with π-electron system. Aminonitropyridines which show the largest red shift of long-wavelength bands for all isomers are a special case. Some aspects of their electronic transitions were discussed previously.[9,11a] Moreover, the hydrogen bonding effect for planar π-bonded groups[4] (NO_2, CO_2Et and $CONH_2$) may influence the spectra.[4,5,9] It seems that tautomeric equilibria are not responsible for the feature of electronic spectra since the fairly constant

TABLE 3

Spectral Parameters[a] of 3-Substituted 2-Aminopyridines (Series 3)

R	Observed		Found (Gaussian Analysis)					
			Band I			Band II		
	$10^3\nu$	logε	$10^3\nu$	logε	$10^{-2}f$	$10^3\nu$	logε	$10^{-2}f$
H	33.69	3.70	35.32	3.48	1.31	33.31	3.61	2.47
Me	33.92	3.67	35.63	3.44	1.66	33.78	3.57	3.34
Cl	32.91	3.76	34.41	3.56	3.05	32.65	3.62	0.71
Br	32.80	3.77	33.86	3.62	2.39	32.25	3.60	0.45
OMe	33.61	3.81	35.09	3.55	3.06	33.31	3.74	7.55
CO_2Et	29.93	3.93	31.36	3.72	2.32	29.54	3.82	4.55
NO_2	25.91	3.91	27.64	3.66	2.42	25.54	3.81	3.97
NH_2	see Table 1							
NHMe	32.16	3.95	34.03	3.62	2.18	31.87	3.85	5.97
NHAc	32.41	3.92	34.24	3.61	2.31	32.16	3.82	4.98

[a]See Table 1.

^{15}N NMR chemical shift of the pyridine nitrogen in substituted aminopyridines excludes the prevalence of pyridinium ions.[19]

Ab initio calculations[20] carried out for 2-, 3- and 4-aminopyridines support a more effective conjugation of the 4-amino nitrogen to the ring π-electron system. They show that total nitrogen charge populations are nearly constant for both ring and amino group nitrogens and the latter being some 0.1 electron greater than the former. However, the σ and π populations clearly discriminate between the two classes of nitrogen. The π-electron populations of amino group nitrogen are some 0.5 electron the ring one and close to a value of 2. The substituent present may differentiate, of course, the ratio of π and σ charge.

TABLE 4

Spectral Parameters[a] of 3-Substituted 4-Aminopyridines (Series 4)

R	Observed		Found (Gaussian Analysis)					
			Band I			Band II		
	$10^3\nu$	logε	$10^3\nu$	logε	$10^{-2}f$	$10^3\nu$	logε	$10^{-2}f$
H	37.05	3.60				36.99	3.60	0.70
Me[b]	37.40	3.68	41.02	4.03	12.64	37.21	3.65	1.12
OMe[b]	36.72	3.69	40.52	4.20	15.51	36.69	3.52	0.99
F[b]	36.76	3.62	41.32	4.21	29.56	36.79	3.48	0.78
Cl[b]	35.55	3.74	40.78	4.03	9.96	35.89	3.18	0.16
Br[b]	35.50	3.34	40.64	3.93	5.98	35.37	3.24	0.23
CO_2Et	32.33	3.66	34.73	3.26	0.51	32.45	3.57	1.13
NO_2	27.99	3.77	30.31	3.47	1.19	27.84	3.68	3.70
NH_2				see Table 2				
NHMe[c]	33.35	3.74	38.17	3.47	0.99	33.10	3.67	4.73
	38.24	3.55						
NMe_2[d]	35.10	3.58	38.38	3.00	0.15	35.17	3.10	1.24
	39.95	3.28	43.48	3.68	2.91			

[a]See Table 1; [b]Observed band is the shoulder of the band at 40810 cm^{-1} (logε = 4.10) for Me, 45500 cm^{-1} (logε = 4.15) for OMe, 41280 cm^{-1} (logε = 4.27) for F, 40620 cm^{-1} (logε = 4.08) for Cl, 41440 cm^{-1} (logε = 4.03) for Br; [c]The short-wavelength band is the shoulder; [d]Both observed bands are the shoulders of the band at 43580 cm^{-1} (logε = 4.14).

TABLE 5

CNDO/S Calculations[a] of Electronic Transitions in Aminopyridines

2-aminopyridine		3-aminopyridine		4-aminopyridine	
$10^3\nu$	$10^{-2}f$	$10^3\nu$	$10^{-2}f$	$10^3\nu$	$10^{-2}f$
35.12	0.56	34.66	0.47	35.76	0.48
37.44	8.90	36.96	8.82	38.32	1.41
46.38	25.70	46.59	24.05	47.28	0.47
47.49	0.42	47.31	0.67	47.58	33.61

[a]For ν and f see Table 1

The availability of the substituent for the π-electron system plays an essential role in setting the energy of spectral transition under consideration. In the case of the long-wavelength band, for electron-acceptors the energy increases and for electron-withdrawings decreases. Such a regularity is related to a charge at the atom attached to position 2 of the pyridine moiety. On the other hand, it could be supported by CNDO calculations of energy transition of the first excited state for 2-substituted pyridines (R = Me, OMe, NMe_2, F, CN, CO_2Me and NO_2).[21]

In order to interpret the long-wavelength band the singlet exited states of 17 aminopyridines are studied by the CNDO/S method.[13] The calculations[22] show that the higher excited state, insensitive almost to the substituent, is of a π-π^* nature according to the magnitude of its oscillator strength, f. However, contributions of low-intensity transitions were found (see Table 5, for the respective results in 2-, 3- and 4-aminopyridines). The data calculated show (Tables 5 and 6) that two different transitions are responsible for the long-wavelength band. They differ essentially in their oscillator strength. As expected, the major difficulty lies in the assignment of their character. Among them that of higher f

TABLE 6

CNDO/S Calculations[a] of Electronic Transitions for the Long-Wavelength Band in Substituted Aminopyridines

R	$10^3\nu$	$10^{-2}f$	R	$10^3\nu$	$10^{-2}f$	R	$10^3\nu$	$10^{-2}f$
Series 1								
Me	35.16	1.97	OMe	35.76	11.38	NHMe	35.68	9.83
	36.78	8.82		36.12	1.64		36.21	2.50
NMe_2	35.68	8.67	CO_2Et	34.05	0.46	NO_2	24.70	0.00
	36.36	3.43		35.19	12.39		25.39	0.03
NH_2	34.52	9.19	CN	34.24	17.34		33.13	19.55
	36.53	1.86		34.73	1.76		35.39	0.24
Series 2						Series 3		
NO_2	24.76	0.01	OMe	36.27	3.58	NO_2	24.15	0.00
	25.20	0.02		36.42	2.15		25.80	0.01
	31.32	17.51					32.45	10.98
	34.04	0.21					35.80	0.50
Series 4								
NO_2	24.25	0.00	OMe	36.28	3.58	NHMe	35.65	0.38
	25.98	0.01		38.42	21.50		36.97	2.66
	36.74	3.55						
	37.74	0.40						

[a]For ν and f see Table 1

value could be attributed to a π-π^* transition. However, there is a question about the nature of the second one of lower f value. Consequently, the latter band is not always the lowest-energy transition in the molecule. In the observed spectra it is obscured by the stronger π-π^* transition. The results for aminonitropyridines require more attention. Their two lower energy bands forbidden (see Table 6), perhaps because of a n-π^* nature, are due to the excita-

tion of the NO_2 group itself.[21] The successive two transitions calculated correspond probably to the long-wavelength band observed.

Since a common feature of the spectra under study is the overlap of electronic transitions, the Gaussian analysis was carried out[15] on the long-wavelength band (see data for Band I and II in Tables 1 - 4). Unfortunately, the correspondence between the frequencies obtained on this basis and those found theoretically is not very satisfactory. Moreover, the differences between the oscillator strengths of bands found on the basis of the Gaussian treatment diminish as compared to those found from CNDO/S calculations. It may be attributed to a solvent polarity as well as to some interactions typical of the vicinally substituted system.[4,5,22,23] However, the relationship of frequencies calculated *vs* those obtained from the Gaussian analysis, for Series 1, is of the straight-line character. Thus, for the transition of higher f values the results are as follows: correlation coefficient, $r = 0.949$ and standard deviation, $s = 503$ for number of points, $n = 9$. Worse results of such an identity criterion for the band of lower f values seem to indicate a strong perturbation coming from particular properties of so-called planar π-bonded groups[4,24] *i.e.* NO_2 and CO_2Et ones. The corresponding results are: $r = 0.872$ and $s = 533$ for $n = 8$ (NO_2 is excluded, CO_2Et is the most unfited point).

The duall substituent parameter approach (DSP):[25]

$$\nu_{max} = \rho_I\sigma_I + \rho_R\sigma_R + C$$

quite well explains the substituent effect on the transitions of lower oscillator strength resulted from the Gaussian analysis. The correlation results are compiled in Table 7. The largest deviations are observed for OMe, NH_2 and NO_2 substituents. Some conformational changes can explain a worse fit of OMe moiety.[4,5] For the NO_2 group the easy excitation of the group itself[18,21] is possible. It seems that the major responsibility lies in the lack of the additivity of the spectra studied, which is clearly evident for two NH_2 moieties present. The magnitudes of ρ_R and ρ_I indicate that the electronic transitions studied are controlled by the inductive character of

TABLE 7

DSP Correlations[a] of the Long-Wavelength Band Frequencies[b] in Substituted Aminopyridines

No	Correlation	λ	r	s	F	n
1	$-2.27\sigma_I - 3.07\sigma_{R^o} + 32.98(x10^3)$	1.35	0.969	271	123	10[c]
2	$-8.96\sigma_I - 4.49\sigma_{R^+} + 32.90(x10^3)$	0.50	0.989	649	280	8
3	$-8.62\sigma_I - 2.65\sigma_{R^-} + 35.02(x10^3)$	0.31	0.965	711	96	10
4	$-5.28\sigma_I - 4.66\sigma_{R^-} + 36.56(x10^3)$	0.88	0.978	568	142	11

[a] σ_I, σ_{R^o}, σ_{R^+} and σ_{R^-} parameters were taken from ref.[27]; λ means ρ_R/ρ_I in the DSP equation; r, correlation coefficient; s, standard deviation; F, test for the significance of correlation; n, number of points; [b] Frequencies of the transition obtained from the Gaussian analysis of lower oscillator strength were correlated (see Tables 1 - 4); [c] NO_2 and OMe are rejected.

the group, except for Series 1 when the contribution of the resonance term is more important. This could be due to the strong substituent influence upon the nitrogen ring atom in the excited state. Nevertheless, the almost comparably competitive effect of both localized and delocalized electronic substituent effects could be postulated for all the Series studied.

It should be mentioned that for another combination, *i.e.* the bands taken directly from the spectrum and those of higher f value resulted from the Gaussian analysis, r is < 0.6 -0.7. Moreover, it seems that many deviating points are accidental. The other models like those involved steric parameters or used with success in the case of substituted benzenes did not improve significantly the correlations.[24-26] Moreover, no reasonable results were obtained with intensities as well as oscillator strengths.

It seems that bands which follow the DSP treatment belong to the electronic transitions of comparable character. This may be explained as being attributed to the equally competitions of variable effects responsible for the band under consideration. It may be stated that the electronic effect itself understood as a field/inductive and resonance one is suitable for estimating the substituent influence on the long-wavelength band of aminopyridines studied. If the same equation is employed to interpret the more intense transition according to the f value, the results are much worse. This could be attributed to non-comparable contributions for all substituents[3,9,10] from intramolecular charge-transfer configuration to the band discussed.

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