CROATICA CHEMICA ACTA CCACAA 63 (2) 187—192 (1990)

CCA-1933

YU ISSN 0011-1643
UDC 547.545
Original Scientific Paper

Steric Effects in the UV-Visible Spectra of Benzylideneanilines. Part V.[1] Substituent Effect in the Spectra of 1-(4'-Dimethylaminobenzylideneamino)pyridinium Perchlorates

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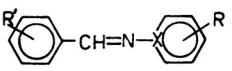
Received July 24, 1989

The electronacceptor substituents in the pyridine ring of 1-(4'-dimenthylaminobenzylideneamino)pyridinium perchlorates cause a red shift of the longest-wavelength UV-Visible absorption band. The electrondonor substituents act in the opposite direction. For the compounds studied a linear relationship between $\tilde{\nu}_{max}$, as well as log ε_{max}, of that band and Hammett δ constants was found.

INTRODUCTION

Benzylideneanilines, due to their non-coplanarity, have always been of great interest to chemists. Their 1-*aza* derivatives (1, X=N$^{\oplus}$) also have twisted molecules, which was confirmed by the



(1)

spectral analysis[1] and theoretical calculations.[2] The results (MINDO/3) also show that Θ_N, *i.e.* the angle of twist between the —CH=N— plane and the N-linked ring, is much larger in carbocyclic derivatives (1, X = C, R, = = *p*-NMe_2).[2]

The effect of the substituent present in the pyridine ring of 1-(benzylideneamino)pyridinium salts on their UV-Visible absorption spectra is not known. In the preceding paper[1] only some 2-mono- and 2,6-dialkyl substituted 4'-dimethylamino derivatives (1, X=N$^{\oplus}$$ClO_4^{\ominus}$, R'=*p*—$NMe_2$) were studied. It was found that monosubstituted and unsubstituted compounds have very similar spectra.[1] However, the intensity of the longest-wavelength absorption band (LWB) in the spectra of disubstituted derivatives is decreased. One can assume that it results from an increased value of the angle of twist. In the present paper, the effect of various substituents in the pyridine ring on UV-Visible spectra of compounds (1, R' = 4'-NMe_2) is discussed. The substituents present in the molecule can be identified by the numbers given in Table I.

TABLE I

Melting ranges of 4'-dimethylaminobenzylidene derivatives of 1-aminopyridinium perchlorates (see formula (1, X—N⊕ ClO$_4$⊖, R' = p—NMes$_2$).

No	R	M. p. / °C	No	R	M. p. / °C
1	2—CN	181—187	*15*	3—$CONH_2$	172—212
2	2—CO_2Et	130—138	*16*	3—COMe	172—212
3	2—COPh	188—211	*17*	3—Br	198—207
4	2—COMe	190—203	*18*	3—F	204—211
5	2—Br	167—179	*19*	3—Me	184—192
6	2—Cl	185—194	*20*	3—NMe_2	198—205
7	H	a	*21*	4—CN	213—223
8	2—Me	a	*22*	4—CO_2Me	195—205
9	2—OMe	129—134	*23*	4—COPh	205—215
10	2—Br, 6-Me	187—191	*24*	4—Et	195—198
11	2—Cl, 6—Me	192—195	*25*	4—t-Bu	228—246
12	3—NO_2	211—222	*26*	4—SMe	211—223
13	3—CN	225—230	*27*	4—OMe	190—198
14	3—CO_2Et	160—175	*28*	4—NMe_2	215—222

[a] See ref. 1

EXPERIMENTAL

Spectroscopic Measurements

The UV-Visible spectra were recorded in the same conditions as before.[1] ^{1}H-NMR spectra were obtained at 100 MHz on a Tesla BS 567 A spectrometer in CF_3COOD and DMSO-d_6.

Compounds

1-Aminopyridinium tosylates were obtained by standard methods[3—6]. Then, the tosyl anion was substituted by the perchlorate one using 70% perchloric acid[4—6]. In some cases the anion exchange was a two-step process: $TsO^- \rightarrow Cl^- \rightarrow ClO_4^-$. A strongly basic Amberlite or Dowex in water were used in the first step. The obtained aqueous solution of the chloride was then acted upon by the equimolar quantity of silver perchlorate.[7] The precipitated silver chloride was filtered off and the filtrate evaporated to dryness giving crude 1-aminopyridinium perchlorate. The final 1,4$_9$[9]-dimethylaminobenzylidaneauino pyridinium perchlorates were obtained like before[1]. They were purified by crystallization from methanol or ethanol. The yields were 60—90%. Although they do not melt sharply, due to the liquid crystal properties[1], satisfactory results of analyses of C, H and N were obtained for all compounds studied (see Table I).

RESULTS AND DISCUSSION

The band at *ca* 1610 cm^{-1} (C=N) was observed in the IR spectra. Typical bands at *ca* 1100 cm^{-1} (wide) and 625 cm^{-1} confirm the presence of the perchlorate anion[1,8,9].

The singlet of azomethine proton in the ^{1}H-NMR spectra of compounds of the formula (1, X=N⊕ClO$_4$⊖, R'=4'—NMe_2) is observed at δ *ca* 9.0 for solutions both in CF_3COOD and DMSO-d_6. The 4'-dimethylamino protons resonate at δ *ca* 3.60 and 3.09 in these solvents, respectively. This shift is almost constant for compounds (1) containing different substituents in the pyridine ring. These spectra will be discussed in detail in our next paper.

Band I (see Table II) in the spectra of the studied perchlorates does not result from local electron excitation in the benzylidene part of the molecule.

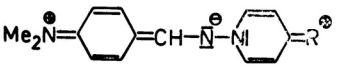
TABLE II

Spectral parameters of 1-(4'-dimethylaminobenzylideneamino)pyridinium perchlorates in MeOH. The numbers in brackets represent the shoulders

N°	Band I		Band II		Band III		Band IV	
	$\tilde{\nu}_{max}$ [kK]	$\log\varepsilon^a$	$\tilde{\nu}_{max}$ [kK]	$\log\varepsilon^a$	$\tilde{\nu}_{max}$ [kK]	$\log\varepsilon^a$	$\tilde{\nu}_{max}$ [kK]	$\log\varepsilon^a$
1	23.0	3.65	29.9	4.00	(32.2)	(3.95)	39.0	4.08
2	23.7	4.30	(28.4)	(4.07)	(31.8)	(3.91)	38.2	4.04
3	24.4	4.40	—	—	33.2	3.92	39.0	4.13
4	24.4	4.19	—	—	35.0	3.86	38.4	4.11
5	25.5	4.34	(29.2)	(4.01)	32.1	3.86	39.4	3.94
					33.6	3.86		
6	25.8	4.33	(29.3)	(4.01)	32.2	3.85	39.6	3.93
					33.5	3.85		
7	24.6[b]	4.46[b]	—	—	32.8[b]	3.87[b]	39.1[b]	4.05[b]
8	25.5[b]	4.47[b]	—	—	32.9[b]	3.83[b]	39.1[b]	4.05[b]
9	26.5	4.46	(29.8)	(3.96)	(32.2)	(3.83)	41.2	3.95
					34.0	3.94		
10	26.3	4.46	—	—	32.2	3.79	40.4	3.94
					34.9	4.04		
11	26.3	4.42	—	—	32.2	3.82	40.4	3.94
					34.9	4.00		
12	22.8	4.29	29.7	4.01	(32.5)	(3.87)	(39.0)	(3.98)
13	23.1	4.26	(28.5)	(4.05)	(31.8)	(3.90)	37.6	3.83
14	23.9	4.37	(29.1)	(3.96)	32.0	3.89	38.2	3.94
15	23.8	4.36	30.0	3.92	(31.9)	(3.89)	38.6	3.95
16	24.0	4.31	(29.6)	(3.89)	32.0	3.83	38.4	3.89
17	23.5	4.37	29.9	3.98	(31.9)	(3.94)	37.2	3.95
18	24.4	4.28	28.4	4.16	(31.8)	(3.98)	39.2	4.04
19	24.8	4.44	—	—	32.8	3.74	38.8	3.89
20	25.7	4.50	—	—	33.4	3.89	38.4	4.21
21	21.4	4.22	29.0	4.15	(36.0)	(4.00)	37.4	4.04
22	21.8	4.30	29.2	4.18	(32.2)	(3.91)	37.2	3.98
23	23.2	4.31	29.0	4.10	(32.8)	(3.94)	37.6	4.04
24	24.9	4.49	—	—	33.0	3.84	39.2	4.03
25	24.8	4.50	—	—	33.1	3.84	39.1	4.04
26	24.3	4.55	—	—	31.8	4.17	(38.6)	(3.60)
27	25.6	4.57	—	—	(33.0)	(3.82)	38.7	3.97
28	25.9	4.63	—	—	(31.7)	(4.10)	40.2	4.00
					33.1	4.18		

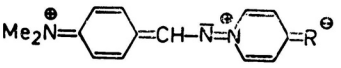
[a] ε denotes the extinction coefficient [$M^{-1} \cdot cm^{-1}$]
[b] Taken from ref. 1

This conclusion can be drawn from the analysis of their spectra as compared with those of the respective hydrazonium salts p—Me_2N—C_6H_4—CH=N—$\overset{\oplus}{N}R_3$, where R=alkyl and/or H[1,10]. Thus, the resonance interaction between the C=N bond and the pyridine ring really does take place in the compounds studied[11]. One can expect rather a large angle of twist in the molecules of compounds carrying electrondonor substituents in the pyridine ring (for such compounds LWB appear at shorter waves, see Table II). The *sp* hybridization of the azomethine nitrogen atom will be more apreciable in molecules of such derivatives:



(2)

The electronwithdrawing substituents will favour the intramolecular charge-transfer and will force the molecule to be more planar by creating the long-distance conjugation:



(3)

The data in Table III are the relative positions of band I. It shows the effect of the same substituents appearing in different positions of the pyridine ring upon the spectrum. The changes are comparable for compounds carrying the electronwithdrawing groups in positions 2 and 3, and the electrondona-

TABLE III

Relative position of LWb, in kK, in the spectra of 1-(4' - dimethylaminobenzylidene-amino) pyridinium perchlorates (1), X=N⊕C10⊖4, R'=p—NMe2

R	$\Delta\tilde{\nu} = \tilde{\nu}^{R}_{max} \cdot 10^{-3} - 24.6$ 2—	3—	4—
CN	—1.6	—1.5	—3.2
CO_2Alk^a	—0.9	—0.7	—2.8
COPh	—0.2	—	—1.4
Br	O.9	—1.1	—
Alk[a]	0.9	0.2	0.3
OMe	1.9	—	1.0
NMe_2	—	1.1	1.3

[a] Alk = Me, Et

ting ones in positions 3 and 4. Moreover, the same substituent is a stronger acceptor in position 4 than in position 2. There is a reverse situation for electrondonor groups. It seems that such substituents appearing in position 2, which is closer to pyridinium N⊕, will be a stronger donor than when it is in the far removed position 4. However, the attraction of the negative charge by the substituent (see structure (3)) will be more effective when it is farther away from the positive charge located at pyridinium N⊕.

Earlier studies[11-15] show that LWB in the spectra of componuds of the formula (1, X = C and N⊕) carrying the constant substituent R' = *p*-NO_2 or *p*-NMe_2, and constant R = H or *p*-NMe_2 is red shifted when the variable substituent is getting more electrondonor or electronacceptor. In general, it is independent of X, R and R'. The only exception is (1, X = N⊕, R' = *p*-NMe_2). In this case the position of LWB and δ Hammett substituent constants[16] (δ_m and δ_p for positions 3 and 4, respectively) changes monotonously (see Figure 1).

Some strong electronacceptor substituents do not follow the relationship. Thus, for 16 correlation points (*i.e.* 4-CO_2Me and 4-CN excluded), the straight line in Fig. 1 has the following parameters intercept 2.5×10^4, slope -2.4×10^3, correlation coefficient 0.948, standard deviation $\pm$ 3.1. This shows that the position of band I depends linearly on the electronic effect

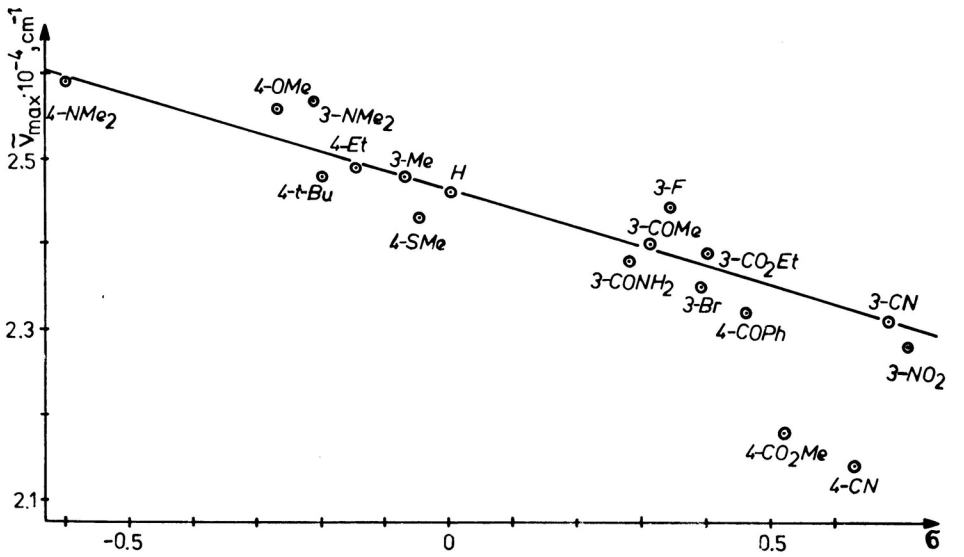


Figure 1. Relationship of ν^{R}_{max} of 1-('4-dimethylaminobenzylideneamino)--pyridiniums *vs* σ values

of the substituent present in the pyridine ring. It seems that Θ_N changes in the same way. Only some strong electronacceptor R's cause particularly high batochromic shifts of band I, and, thus, appreciable diminutions of Θ_N.

Although the band intensity, as opposed to, for instance, the oscillator strength, is not a reasonable spectral parameter, a good linear correlation between log ε_{max} of LWB and σ constants was obtained (computed for 18

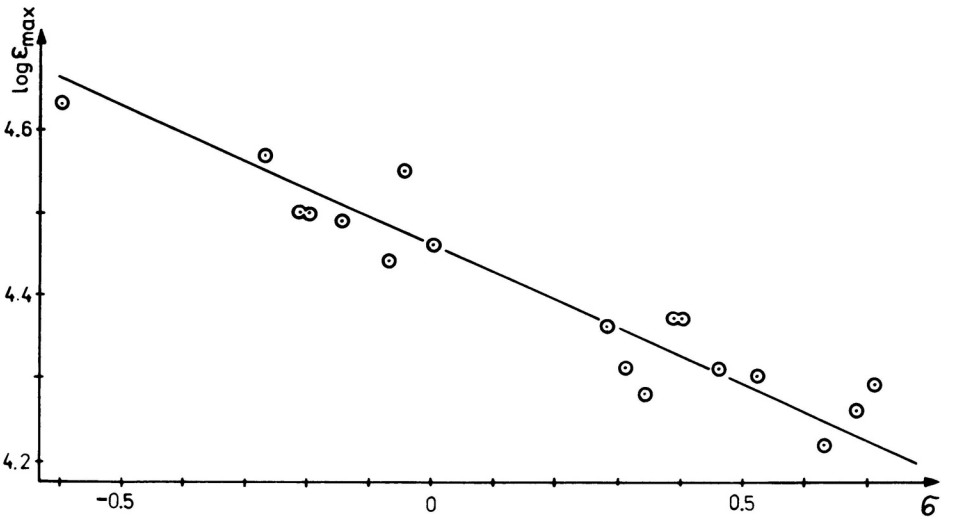


Figure 2. Relationship of log ε^{R}_{max} of 1-(4'-dimethylaminobenzylideneamino)--pyridiniuus *vs* σ values

points: intercept 4.45, slope —0.300, correlation coefficent 0.948, standard deviation $\pm$ 0.040). Unfortunately, it is not possible to predict the Θ_N value, because the intensity of the band depends not only on the molecular geometry but also on the change of the dipol moment during the electron transmission[17]

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SAŽETAK

Sterički učinci u UV/vidljivim spektrima benzilidenanilina. V. Učinak supstituenata u spektrima 1-(4'-dimetilaminobenzilidenamino) piridinijevih perklorata.

R. Gawinecki

Elektron-akceptorski supstituenti u piridinskom prstenu 1-(4'-dimetilaminobenzilidenamino) piridinijevih perklorata prouzrokuju batokromni pomak one UV/VIS apsorpcijske vrpce koja se javlja pri najvećoj valnoj duljini. Očekuje se da će takovi spojevi biti planarnije građe nego li matični, nesupstituirani spoj. Za proučavane spojeve primijećen je linearan suodnos ν_{max} i log ε_{max} s Hammettovom konstantom σ.