ELSEVIER

Dyes and Pigments 45 (2000) 103–107

DYES and PIGMENTS

The effect of the amino group on the spectral properties of substituted styrylpyridinium salts

Ryszard Gawinecki *, Katarzyna Trzebiatowska

Department of Chemistry, Technical and Agricultural University, Seminaryjna 3, PL-85-326 Bydgoszcz, Poland

Received 2 October 1999; received in revised form 16 December 1999; accepted 21 January 2000

Abstract

Thirty-six *trans*-1-methyl-2- and -4-(*p*-aminostyryl)pyridinium perchlorates were obtained by the condensation of dimethylpyridinium salts with *p*-aminobenzaldehydes. In all cases, a strong absorption band was present in their UV/VIS spectra above 400 nm. The spectral parameters were not simply related to the substituent constants of the amino groups. A comparison with the respective styrylpyridinium iodides showed the anion to have no effect on the spectra. The 1-methyl-(*p*-aminostyryl)pyridinium salts prepared are expected to be useful materials in non-linear optics and in biological studies.

Keywords: Styrylpyridinium salts; Knoevenagel condensation; Absorption spectra; Amino groups; Substituent effects; Steric hindrance

1. Introduction

Aminostyrylpyridinium salts have been thoroughly investigated from the point of view of negative solvatochromism [1] and structure–colour relationship [2]. Such dyes have gained increasing interest also because of their potential applicability in non-linear optics, as potential sensors and in physiology/biochemistry areas. The colorants were found useful in studies of the transport mechanisms through cell membranes [3] and voltage-sensitive probes in neurones [4]. Depending on the electrical potential inside and outside the cell, either the charge of the dye within the cell membrane or the dye itself, moves between the aqueous and organic membrane interphase, causing changes in the colorant's optical properties [5,6]. It was found that the combined ion exchange or co-extraction of the analyte ion and the charged indicator between the aqueous and organic interphase was responsible for the analyte-induced signal change [7,8]. The compounds have also found application in the optical sensing of ionic species. Styrylpyridinium salts with significant charge shift between the ground and excited state [9,10] have been shown to exhibit non-linear optical properties [11]. These effects, which can be observed in both solution and in organized systems such as Langmuir-Blodgett layers and crystals, render such dyes promising candidates in the development of optical data storage systems or optical switching devices [12,13].

* Corresponding author. Tel.: +48-52-379-2900; fax: +48-52-373-1160.

E-mail address: gawiner@chem.atr.bydgoszcz.pl (R. Gawinecki).

0143-7208/00/$ - see front matter
PII: S0143-7208(00)00012-7

Hemicyanine dyes, as exemplified by some stilbazolepyridinium salts, have been used as laser dyes [14,15]. 1-Methyl-2-(*p*-dimethylaminostyryl) pyridinium iodide is a powerful sensitizer for green light [16]. The title compounds also show other very interesting properties, namely they become fluorescent upon infrared excitation [14,15]. 1-Alkyl-2- and -4-(*p*-aminostyryl)pyridinium salts have been found to be useful as fluorescent probes in polymerization processes [17,18].

In this work a series of 1-methyl-(*p*-aminostyryl) pyridinium salts was prepared to determine how changes in the electron donor strength of the amino substituent in the benzene ring affect their spectral properties. Studies on the compounds obtained were also expected to be helpful in evaluating the electron donor power of different amino groups [19].

2. Experimental

2.1. General

Absorption spectra for solutions of compounds **1** and **2** in 96% ethanol were recorded on a Varian CARY 3E UV/VIS spectrophotometer. Melting points were measured on a Boetius table and are uncorrected. Purity of the products was checked using thin layer chromatography on silica gel (eluent chloroform:methanol = 5:1). For all compounds prepared, satisfactory elemental analyses were obtained ($\pm 0.30\%$ for C, H and N).

2.2. Reagents

2- and 4-methylpyridines (picolines) as well as some 4-aminobenzaldehydes were commercially available. Other aldehydes used were obtained according to the procedure described in our recent paper [20].

2.3. Synthetic procedures

2.3.1. 1,2- and 1,4-dimethylpyridinium iodides

These well-known compounds were obtained in almost quantitative yield by refluxing solutions of equimolar amounts of picoline and methyl iodide in acetone. The solid products were filtered off, dried in a vacuum desiccator and used directly in the following stages.

2.3.2. 1,2- and 1,4-dimethylpyridinium perchlorates

70% perchloric acid (0.175 mol) was added to a hot solution (50°C) of dimethylpyridinium iodide (0.17 mol) in methanol (60 cm^3). Cooling of the reaction mixture induced precipitation of the desired products as white crystals. Drying in the vacuum desiccator gave 1,2- and 1,4-dimethylpyridinium perchlorates of mp. 154–156°C (yield 84%) and 136–137°C (yield 60%), respectively.

2.3.3. 1-Methyl(p-aminostyryl)pyridinium perchlorates **1b–1r** and **2b–2r**

A mixture of 1,2- or 1,4-dimethylpyridinium perchlorate (0.01 mol), the appropriate 4-aminobenzaldehyde (0.01 mol) and piperidine (5–10 drops) in methanol (20 cm^3) was refluxed for 1–2.5 h and then kept in a refrigerator for 1 day. The solid products were recrystallized from aqueous ethanol to constant mp (Table 1).

2.3.4. 1-Methyl-(p-acetylaminostyryl)pyridinium perchlorates

These compounds were obtained by the condensation of 1,2- and 1,4-dimethylpyridinium perchlorates with *p*-acetylaminobenzaldehyde. The synthetic procedure used was the same as that for the preparation of compounds **1b–1r** and **2b–2r**. 1-Methyl-2- and -4-(*p*-acetylaminostyryl)pyridinium perchlorates were obtained in 42 and 51% yields, respectively. Their mps were 290–295°C (recrystallized from 75% aqueous ethanol) and 304–306°C (recrystallized from 40% aqueous acetone), respectively.

2.3.5. 1-Methyl-(p-aminostyryl)pyridinium perchlorates **1a** and **2a**

A solution of 1-methyl-(*p*-acetylaminostyryl) pyridinium perchlorate (5.64 g, 0.016 mol) in 25% aqueous perchloric acid (32 cm^3) was refluxed for 1 h. The reaction mixture was then cooled and treated with a 10% aqueous solution of sodium hydroxide to raise the pH to 6. The ensuing mixture was heated to dissolve the solid product formed and the resulting solution was cooled in a

Table 1
Yields and melting points for compounds **1** and **2**

	Series **1**		Series **1′**		Series **2**	
	Mp (°C)	Yield (%)	Mp (°C)	Yield (%)	Mp (°C)	Yield (%)
a	270–273	56			282–286	78
b	227–234.5	67			206.5–207	62
c	253–254.5	67	269.5–270[a]	62	216–224.5	68
d	228–232.2	54			201.5–209	68
e	249–250.5	73	244.5–245.5[b]	39	211–214	90
f	[c]	49			229.5–239	53
g	167–176	39			242.5–247	46
h	205–207.5	86	196.5–200	42	211–218.5	83
i	215–225.5	65			267.5–270	65
j	271.5–277.5	48	257–259	20	252.5–262	54
k	228.5–231	65			234.5–237	81
l	164–165	55			205.5–212	83
m	228–235	60			180–204	60
n	223–228	76			261–266	87
o	225–229	73	250.5–252	43	240–252	57
p	175.5–183	42			230–240	62
q	244.5–247	65			239–245.5	53
r	225–227	50			235–242.5	58

[a] 273–274°C [23,25], 282–283°C [1].
[b] 246–247°C [23], 246°C [25].
[c] Melts in the range 229–233.5 °C, then solidifies and melts again at 239–243°C.

refrigerator for 1 day. The precipitated compounds **1a** and **2a** were recrystallized from 75% aqueous ethanol and from 35% aqueous acetone, respectively, to constant mp (Table 1).

*2.3.6. 1-Methyl-2-(*p*-aminostyryl)pyridinium iodides **1′***

These compounds were obtained starting from 1,2-dimethylpyridinium iodide and respective *p*-aminobenzaldehyde using the procedure described in Section 2.3.3. The products were purified by their recrystallization from 75% aqueous ethanol. The yields and mp. of the compounds are shown in Table 1.

3. Results and discussion

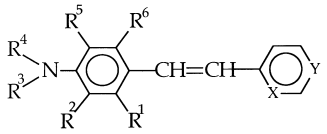
3.1. Synthetic strategy

Due to the presence of active methyl groups in the 2- and 4-methylpyridines, these compounds react with benzaldehydes to give the respective styrylpyridines [21,22]. These can be easily transformed into 1-alkylstyrylpyridinium salts by treatment with alkyl halides [21]. Alternatively, the same products are also obtained directly from 1,2- and 1,4-dimethylpyridinium salts and benzaldehydes in the presence of base [1,21,23–27]. In the latter case the secondary alcohol initially formed loses a water molecule to give the 1-methylstyrylpyridinium salt [24]. The compounds discussed in this paper are mainly the products of the reaction between 1,2- and 1,4-dimethylpyridinium perchlorates with different *p*-aminobenzaldehydes (Knoevenagel condensation). Since *p*-aminobenzaldehyde itself is not commercially available and is known to be rather unstable [28], the parent 1-methyl-(*p*-aminostyryl)pyridinium salts **1a** and **2a** were obtained by hydrolysis of their acetyl derivatives. The respective iodide has been obtained earlier [27] by reduction of 1-methyl-(*p*-nitrostyryl)-pyridinium iodide with stannous chloride in hydrochloric acid (Scheme 1)

As a hard base, the perchlorate anion has a high ionization potential [29]. To avoid the possibility

of charge transfer from anion to cation [30] in the synthesized compounds, perchlorates were mostly prepared [31].

While the ^1H and ^{13}C NMR spectra of compounds **1** and **2** will not be discussed here [32], it can be stated that, in general, the anion has no effect on the ^1H and ^{13}C chemical shifts. Coupling between protons in the –CH=CH– fragment ($^3J \approx 16$ Hz) indicated that the obtained compounds were the *trans* (*E*) isomers. It is known that the products can be transformed into the *cis* isomer by photolysis of their acidic solutions [27].



1 X = $N^{\oplus}CH_3$ $ClO_4^{\ominus}$, Y = CH

1' X = $N^{\oplus}CH_3$ $I^{\ominus}$, Y = CH

2 X = CH, Y = $N^{\oplus}CH_3$ $ClO_4^{\ominus}$

	R^1	R^2	R^3	R^4	R^5	R^6
a	H	H	H	H	H	H
b	H	H	H	CH_3	H	H
c	H	H	CH_3	CH_3	H	H
d	H	H	CH_3	C_2H_5	H	H
e	H	H	C_2H_5	C_2H_5	H	H
f	CH_3	H	CH_3	CH_3	H	H
g	CH_3	H	CH_3	CH_3	H	CH_3
h	H	CH_3	CH_3	CH_3	H	H
i	H	CH_3	CH_3	CH_3	CH_3	H
j	H	H	$(CH_2)_4$		H	H
k	H	H	$(CH_2)_5$		H	H
l	H	H	$(CH_2)_6$		H	H
m	H	$(CH_2)_2$		CH_3	H	H
n	H	$(CH_2)_3$		H	H	H
o	H	$(CH_2)_3$		CH_3	H	H
p	H	$(CH_2)_4$		CH_3	H	H
q	H	$(CH_2)_2$		$(CH_2)_3$		H
r	H	$(CH_2)_3$		$(CH_2)_3$		H

Scheme 1.

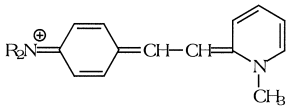
Neutral solutions of (*p*-aminostyryl)pyridinium salts are resistant to light due to the large contribution of the following resonance structure (lack of the ethylene double bond) [27] (Scheme 2).

It is also known [27] that the *cis* isomers of such compounds are not stable: they readily thermally isomerise to the *trans* form [27]. Significant differences of the UV/VIS spectral characteristics of the *cis* and *trans* isomers are notable [27].

It is evident that the melting points for numerous compounds presented in Table 1 were not sharp. This can be attributed to the liquid crystal properties of the styrylpyridinium salts.

3.2. Spectroscopic properties

λ_{max} and log ε values for the main band in the absorption spectra of perchlorates **1** and **2** are shown in Table 2 from which it is apparent that



Scheme 2.

Table 2
Absorption spectra for compounds **1** and **2** (solutions in 95% ethanol)

	Compounds **1**		Compounds **2**	
	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε
a	442	4.38	455	4.39
b	461	4.54	475	4.67
c	464	4.55	477	4.66
d	469	4.59	483	4.65
e	475	4.59	489	4.69
f	468	4.35	486	4.52
g	349	4.05	381	4.36
h	406	4.33	417	4.40
I	397	4.23	402	4.27
j	476	4.56	490	4.70
k	458	4.46	465	4.51
l	477	4.61	491	4.69
m	469	4.44	477	4.46
n	481	3.30	489	3.58
o	483	4.45	498	4.61
p	433	4.35	439	4.42
q	494	4.50	504	4.42
r	505	4.60	518	4.63

the spectra of the iodides **1′** and perchlorates **1** were practically identical ($\Delta\lambda_{max} = 1$ nm, $\Delta\log\varepsilon = 0.03$). Moreover, in their spectra, a weak band at 265–305 nm ($\log\varepsilon = 3.5$–3.9) for compounds **1** and at 260–310 nm ($\log\varepsilon = 3.1$–4.2) for compounds **2**, can be seen. The presence of an additional band at ca 370 nm in the spectra of compounds **1n** and **2n** is noteworthy {**1n**: $\lambda_{max} = 363$ nm ($\log\varepsilon = 4.06$), **2n**: $\lambda_{max} = 377$ nm ($\log\varepsilon = 3.48$)}.

Compounds **1i** and **2i** seem to be unique. Due to the steric influence of two *ortho* methyl groups, the dimethylamino substituent is a very weak electron donor [19]. The λ_{max} values cover a range of 108 and 116 nm ranges for compounds **1** and **2**, respectively. Due to the presence of two methyl groups neighbouring the ethylene bond (steric interaction), compounds **1g** and **2g** are exceptional and were excluded. In both series the julolidinyl derivatives **1r** and **2r** absorb at higher wavelength than all other compounds. The lowest λ_{max} and ε values were obtained for compounds **1i** and **2i**. While the most intense bands appeared in the spectra of compounds **1l** and **2f**, the ε values were only slightly lower than those obtained for many other compounds.

Poor correlation was found between the position of the band and its intensity (Table 2) and σ_R^o substituent constants based on the chemical shifts of the *para* carbon atom in the respective *p*-aminobenzaldoximes [19]. It is apparent that the contribution of the inductive effect for the different amino groups was almost constant [33] and thus σ_R^o substituent constants should be related to the electronic effects of the substituent. However, the UV/VIS spectral data obtained for compounds **1** and **2** and the σ_R^o values were not linearly related to each other. Alternatively, the λ_{max} values in both series were linearly dependent on each other ($r = 0.995$, points for **g** and **n** excluded). Such interrelationship for the band intensities is significantly much worse.

References

[1] Matsui M, Kawamura S, Shibata K, Muramatsu H. Bull Chem Soc Japan 1992;65:71.
[2] Hünig S, Rosenthal O. Liebigs Ann 1955;592:161.
[3] Lehmann F, Mohr GJ, Czerney P, Grummt U-W. Dyes Pigm 1995;29:85 (and papers cited therein).
[4] Fromherz P, Dambaher KH, Ephardt H, Lambacher A, Müller CO, Neigl R, Schaden H, Schenk O, Vetter T. Ber Bunsen-Ges Phys Chem 1991;95:1333.
[5] Waggoner AS. Ann Rev Biophys Bioeng 1979;8:47.
[6] Das TK, Periasamy N, Krishnamoorthy G. Biophys J 1993;64:1122.
[7] Kawabata Y, Tahara R, Kamichika T, Imasaka T, Ishibashi N. Anal Chem 1990;62:1528.
[8] Schaffar BPH, Wolfbeis OS, Leitner A. Analyst 1988;113:693.
[9] Strehmel B, Seifert H, Rettig W. J Phys Chem 1997;101B:2232.
[10] Wandelt B, Turkevitsch P, Stranix BR, Darling GD. J Chem Soc, Faraday Trans 1995;91:4199.
[11] Duan X-M, Okada Sh, Oikawa H, Matsuda H, Nakanishi H. Mol Cryst Liq Cryst 1995;267:89.
[12] Marder SR, Perry JW. Science 1994;263:1706.
[13] He G, Xu Zh. J Phys Chem 1997;101B:2101.
[14] Narang U, Zhao ChF, Bhawalkar JD, Bright FV, Prasad PN. J Phys Chem 1996;100:4521 (and papers cited therein).
[15] Zhao ChF, Gvishi R, Narang U, Ruland G, Prasad PN. J Phys Chem 1996;100:4526 (and papers cited therein).
[16] Hamer FM. The chemistry of heterocyclic compounds. In: Weissberger A, series editor. The cyanine dyes and related compounds. New York: Interscience Publishers, 1964.
[17] Jager WF, Kudasheva D, Neckers DC. Macromolecules 1996;29:7351.
[18] Wróblewski S, Trzebiatowska K, Jędrzejewska B, Pietrzak M, Gawinecki R, Pczkowski J. J Chem Soc, Perkin Trans 2, 1999; 1909.
[19] Gawinecki R, Kolehmainen E, Kauppinen R. J Chem Soc, Perkin Trans. 2, 1998; 25.
[20] Gawinecki R, Andrzejak S, Puchała A. Org Prep Proced Int 1998;30:455.
[21] Kuo KT. J Chinese Chem Soc (Taipei) 1978;25:131.
[22] Parker ED, Furst A. J Org Chem 1958;23:201.
[23] Phillips AP. J Org Chem 1947;12:333.
[24] Kramer DN, Bisauta LP, Bato R, Murr BL. J Org Chem 1974;39:3132.
[25] Phillips AP. J Am Chem Soc 1952;74:3296.
[26] Williams JLR, Adel RE, Carlson JM, Reynolds GA, Borden DG, Ford JA. J Org Chem 1963;28:387.
[27] Williams JLR, Carlson JM, Adel RE, Reynolds GA. Can J Chem 1965;43:1345.
[28] Campaigne E, Bude WM, Schaefer GF. Org Synth Coll 1963;4:31.
[29] Pearson RG, Songstad J. J Am Chem Soc 1967;89:1827.
[30] Rodig OR. In: Abramovitch RA, editor. Pyridine and its derivatives, supplement: part one. New York: Interscience Publication, 1974. p. 309.
[31] Le Noble WJ. Highlights of organic chemistry. An advanced textbook. New York: Marcel Dekker, 1974. p. 848
[32] Aun ChE, Clarkson TJ, Happer DAR. J Chem Soc., Perkin Trans 2 1990; 645.
[33] Effenberger F, Fischer P, Schoeller WW, Stohrer W-D. Tetrahedron 1978;34:2409.