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Dyes and Pigments 60 (2004) 143–145

DYES and PIGMENTS
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# Effect of the amino group on the properties of 1-(benzylideneamino)pyridinium salts

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Received 5 April 2003; received in revised form 2 June 2003; accepted 16 July 2003

## Abstract

Eleven (*E*)-4-*t*-butyl-1-(4-dimethylaminobenzylideneamino)pyridinium perchlorates were obtained by the condensation of 1-amino-4-*t*-butylpyridinium perchlorate with *p*-amino-benzaldehydes. The position of the primary band in their UV/VIS spectra was not simply related to the σ substituent constants of the different amino groups. Only two compounds were found to be fluorescent and piezochromic.

*Keywords:* 1-(Benzylideneamino)pyridinium salts; Substituent effect; Amino groups; Absorption spectra; Piezochromism

## 1. Introduction

1-(Benzylideneamino)pyridinium salts were found to possess both tinctorial and fungicidal properties [1]. The yellow-green leaflets of (*E*)-4-*t*-butyl-1-(4-dimethylaminobenzylideneamino)pyridinium perchlorate have both piezochromic and fluorescence properties [2]. The fluorescence disappeared when the spectrum was recorded in solution. An orange-colored modification of (*E*)-4-*t*-butyl-1-(4-dimethylaminobenzylideneamino)-pyridinium perchlorate was obtained by heating the sample over 180 °C or by simply pressing the yellow-green crystals with, for example, a spatula [2]. Scanning calorimetry (DSC) experiments revealed some polymorphic crystalline changes take place (the solid state $^{13}$C NMR spectra of the yellow-green and orange forms were identical) [2]. The orange crystals were stable for several hours although on longer standing, the original form was reversibly recovered [2].

It is worth mentioning that (*E*)-4-*t*-butyl-1-(4-dimethylaminobenzylideneamino)pyridinium perchlorate shows unique behaviour in the series examined (substitution of *t*-butyl by other alkyls, e.g. methyl, ethyl or *i*-propyl, annihilates both piezochromy and fluorescence [2,3]). This prompted us to search other compounds of this type.

## 2. Experimental

### 2.1. General

Melting points were measured on a Boetius table and are uncorrected. Satisfactory elemental analyses (±0.30% for C, H and N) were obtained

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doi:10.1016/S0143-7208(03)00154-2

for all compounds prepared. Absorption spectra for solutions of compounds **1–11** in methanol were recorded using a Varian CARY 3E UV/VIS spectrophotometer. $^1$H and $^{13}$C NMR experiments were run with a Varian Gemini 2000 spectrometer working at 199.98 MHz for proton and 50.28 MHz for carbon-13 for 0.1–0.2 M solutions in DMSO-$d_6$ at 293 K.

### 2.2. Syntheses

#### 2.2.1. 1-Amino-4-t-butyl-pyridinium perchlorate

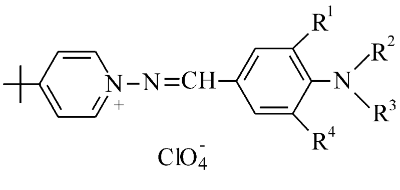
Three millilitres of 70% perchloric acid were added to a solution of 6.45 g (0.02 mol) of 1-amino-4-*t*-butylpyridinium tosylate [4,5] in the minimum amount of hot methanol. The white solid obtained after freezing of the reaction mixture was recystallized from methanol to give 1-amino-4-*t*-butylpyridinium perchlorate which melted at 110–113 °C.

#### 2.2.2. (E)-4-t-butyl-1-(4-aminobenzylideneamino) pyridinium perchlorates {(E)-1-[(4-amino-phenyl) methyleneamino]pyridinium perchlorates}

A mixture of 2.51 g (0.01 mol) of 1-amino-4-*t*-butylpyridinium perchlorate, 0.01 mole of the respective *p*-aminobenzaldehyde [6], 20 ml of 95% ethanol and 10 drops of 70% perchloric acid was refluxed for 1–2 h. The reaction products were precipitated from the cold reaction mixture by adding diethyl ether and were recrystallized from methanol.

## 3. Results and discussion

The synthetic procedure for (*E*)-4-*t*-butyl-1-(4-dimethylaminobenzylideneamino)-pyridinium perchlorates (Scheme 1) was that used before [7,8]. The reaction yields were not high (Table 1). The liquid crystal properties of the compounds studied were probably responsible for their wide melting ranges (Table 1). Both $^1$H and $^{13}$C NMR spectra support the structures of the obtained compounds. The chemical shifts of the azomethine proton and carbon atom were 8.74–8.91 and 166.74–167.67 ppm, respectively. UV/VIS spectral parameters for the compounds studied are shown in Table 2. While the pyridine ring in the compounds studied seems to be unaffected by the amino substituent (Scheme 2), steric effects caused by the R$^1$ group lowered the electron-donor ability of the amino group. In consequence, the intramolecular charge transfer in **5** was less effective than in **2**. In contrast, the effect of the alkane bridge(s) R$^1$/R$^2$ (R$^3$/R$^4$) was not known. The data in Table 2 show that the nitrogen atom in **9**, and especially in **10** and **11**, has much stronger electron-donor properties that that in **2**. A similar effect of the 1-pyrrolidino substituent in compound **6** seems also noteworthy.



Scheme 1.

Unfortunately, the position of the primary band ($\lambda_{\max}$ 385–440 nm) was not linearly related to $\sigma_p$ constants [9], however, the values of $\lambda_{\max}$ of the long-wavelength band in the spectra of the compounds studied changed in the following order:

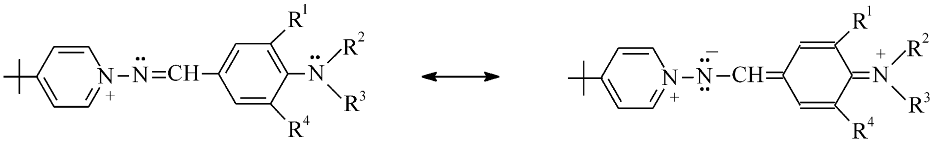
$$\mathbf{11} > \mathbf{10} > \mathbf{9} > \mathbf{6} = \mathbf{4} > \mathbf{3} > \mathbf{7} > \mathbf{2} > \mathbf{8} = \mathbf{1} > \mathbf{5}$$

The positions of such band in the spectra of (*E*)-1-methyl-4-(*p*-aminostyryl)pyridinium perchlorates carrying the same substituents [10,11] changed in a similar order.

Table 1
Yields and melting points for compounds **1**–**11**

| | R$^1$ | R$^2$ | R$^3$ | R$^4$ | mp (°C) | Yield (%) |
|---|---|---|---|---|---|---|
| **1** | H | Me | H | H | 211–218 | 39 |
| **2** | H | Me | Me | H | 228–246[a] | – |
| **3** | H | Me | Et | H | 183–187 | 66 |
| **4** | H | Et | Et | H | 154–165 | 57 |
| **5** | Me | Me | Me | H | 124–133 | 65 |
| **6** | H | $(CH_2)_4$ | | H | 187–209 | 59 |
| **7** | H | $(CH_2)_5$ | | H | 174–179 | 63 |
| **8** | $(CH_2)_3$ | | H | H | 199–213 | 48 |
| **9** | $(CH_2)_3$ | | Me | H | 187–195 | 44 |
| **10** | $(CH_2)_2$ | | $(CH_2)_3$ | | 151–160 | 46 |
| **11** | $(CH_2)_3$ | | $(CH_2)_3$ | | 173–182 | 44 |

[a] Ref. [8].



Scheme 2.

Table 2
Absorption spectra for compounds **1**–**11** (solutions in methanol)[a]

| | $\lambda_{max}$ [nm] log $\varepsilon_{max}$ | | | |
|---|---|---|---|---|
| **1** | 254 | 300.5 | – | 398.5 |
| | 4.08 | 3.84 | – | 4.47 |
| **2** | 256 | 302 | – | 403 |
| | 4.04 | 3.84 | – | 4.50 |
| **3** | 256 | 304 | (314) | 408 |
| | 4.08 | 3.86 | (3.83) | 4.50 |
| **4** | 258.5 | 305 | (325) | 413 |
| | 4.06 | 3.89 | (3.81) | 4.52 |
| **5** | 258.5 | – | – | 384.5 |
| | 4.16 | – | – | 4.31 |
| **6** | 257.5 | 303 | (313.5) | 413 |
| | 4.09 | 3.91 | (3.87) | 4.52 |
| **7** | 257 | 306.5 | – | 406.5 |
| | 4.10 | 3.85 | – | 4.49 |
| **8** | 254.5 | 301 | – | 398.5 |
| | 4.08 | 3.87 | – | 4.49 |
| **9** | 260.5 | (307) | 317.5 | 420 |
| | 4.08 | (3.79) | 3.81 | 4.46 |
| **10** | 262 | – | 331 | 435 |
| | 4.10 | – | 3.77 | 4.38 |
| **11** | 260.5 | (312) | (325) | 438.5 |
| | 4.07 | (3.71) | (3.78) | 4.42 |
| | (276) | | (347) | |
| | (3.97) | | (3.83) | |

[a] Shoulders are given in parentheses.

Of the compounds studied only **2** and **4** were found to be fluorescent and piezochromic (these properties in **4** were less obvious). It is noteworthy that 1-(benzylideneamino)pyridinium perchlorates carrying various non-amino substituents in the benzene ring did not reveal these properties [7,8] which is believed to result from a special crystal packing only [2].

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