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# The Synthesis of Some Hetarylazopyridone Dyes and Solvent Effects on Their Absorption Spectra

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## *ABSTRACT*

*The synthesis of hetarylazopyridone dyes by coupling 1-butyl-3-cyano-6-hydroxy-4-methyl-2(1H)pyridone with diazotized aminothiazoles and aminobenzothiazoles is reported. Visible absorption spectra of the dyes were examined in various solvents and the compounds in solution exhibited hydrazone–common anion equilibrium. The hetarylazopyridones readily undergo acid dissociation into the common anion in methanol, DMF and DMSO. The effect of temperature on the visible absorption spectra is also discussed.*

## 1 INTRODUCTION

In the last two or three decades disperse dyes derived from the use of aromatic heterocyclic compounds as diazo or coupling components have gained importance. A large number of patent specifications exist in which either the diazo or coupling component is heterocyclic. The literature on disperse dyes based on heterocyclic diazo components has been summarized in reviews by Butler[1] and by Weaver and Shuttleworth,[2] but these do not report specific data relating to general procedures and yields. Peng *et al.*[3,4] reported a series of compounds prepared by coupling pyridones with diazotized aminothiadiazoles and 2-aminothiazoles, but they did not mention the diazotization conditions used or yields obtained. Peters and Gbadamosi[5] have synthesized disperse dyes by diazotizing aminothiazoles, benzothiazoles, thiadiazoles and thiophenes in nitrosyl

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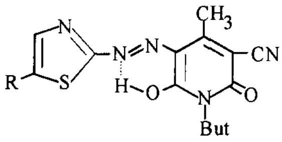
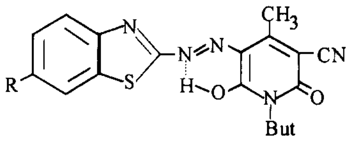


(1)
1a : R = H
1b : R = $NO_2$



(2)
2a : R = H
2b : R = $NO_2$
2c : R = $OCH_3$

sulphuric acid and coupling to N-substituted anilines, reporting yields of crude dyes in the range 82–98%.

In this present work, some new azopyridone dyes (**1a** and **1b**, **2a-c**) were prepared by coupling 1-butyl-3-cyano-6-hydroxy-4-methyl-2(1H)-pyridone with diazotized 2-aminothiazoles and 2-aminobenzothiazoles; solvent effects on the visible absorption spectra of these dyes were examined.

## 2 EXPERIMENTAL

1-Butyl-3-cyano-6-hydroxy-4-methyl-2(1H)pyridone was prepared from ethyl acetoacetate and N-butylcyanoacetamide using the method described in the literature.[6] 2-Aminothiazoles and 2-aminobenzothiazoles were of chemical grade and used without further purification. The solvents used were spectroscopic grade.

IR spectra were determined in KBr and in $CHCl_3$ with a Nicolet 510 FT/IR spectrophotometer. $^1H$ NMR spectra were recorded on a Varian EM 60 spectrophotometer in $CDCl_3$, with TMS as internal reference. Electronic spectra were measured on a Bausch and Lomb Spectronic 2000 spectrophotometer.

### 2.1 General procedure

The preparation of 1-butyl-3-cyano-6-hydroxy-4-methyl-5-(2-thiazolylazo)-2(1H)pyridone is given as illustrative; all other dyes were prepared in a similar manner. Characterization data are shown in Tables 1 and 2.

*Preparation of 1-butyl-3-cyano-6-hydroxy-4-methyl-5-(2-thiazolylazo)-2(1H)-pyridone*
2-Aminothiazole (0·29 g, $2 \times 10^{-3}$ mole) was dissolved in hot glacial acetic acid (2·4 ml) and was rapidly cooled in an ice–salt bath to −5°C. The liquor was then gradually stirred into a cold solution of nitrosyl

**TABLE 1**
Spectral Data for Dyes **1** and **2**

| *Dye* | *IR ($cm^{-1}$) in KBr* | | | *$^1H$ NMR (ppm) in $CDCl_3$* |
|---|---|---|---|---|
| | $\vartheta_{C=O}$ | $\vartheta_{C\equiv N}$ | $\vartheta_{N\text{-}H}$ | |
| **1a** | 1700, 1630 | 2225 | 3110 | 0·7–1·9 (7H, m), 2·5 (3H, s), 4–0 (2H, t), 7·5 (1H, d), 7·6 (1H, d) |
| **1b** | 1700, 1650 | 2220 | 3110 | 0·8–1·8 (7H, m), 2·6 (3H, s), 4·0 (2H, t), 8·5 (1H, s) |
| **2a** | 1695, 1630 | 2215 | 3100 | 0·5–1·7 (7H, m), 2·5 (3H, s), 3·9 (2H, t), 7·1–7·9 (4H, m) |
| **2b** | 1700, 1630 | 2225 | 3090 | 0·6–1·7 (7H, m), 2·6 (3H, s), 3·9 (2H, t), 8·1–8·7 (3H, m) |
| **2c** | 1700, 1640 | 2225 | 3100 | 0·6–1·8 (7H, m), 2·6 (3H, s), 3·9 (2H, t), 3·6 (3H, s), 7·2–8·1 (3H, m) |

sulphuric acid (prepared from sodium nitrite (1 g) and concentrated sulphuric acid (7 ml) at 70°C). After diazotization was complete, the diazo liquor was slowly added to a vigorously stirred solution of 1-butyl-3-cyano-6-hydroxy-4-methyl-2(1H)pyridone (0·412 g, $2 \times 10^{-3}$ mole) in potassium hydroxide (0·112 g, $2 \times 10^{-3}$ mole) and water (2 ml), and the mixture was then stirred for a further 30 min. The solution was partly neutralized with KOH and the precipitated orange solid filtered, washed with cold water and dried. Recrystallization from chloroform gave orange needles (yield 55%).

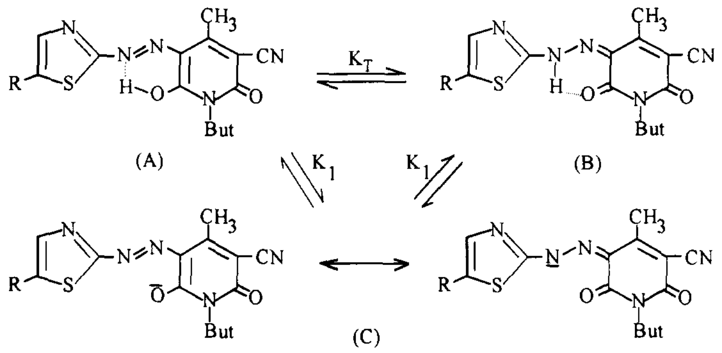
## 3 RESULTS AND DISCUSSION

The hetarylazopyridone dyes **1a** and **1b** and **2a-c** were prepared by coupling 1-butyl-3-cyano-6-hydroxy-4-methyl-2(1H)pyridone with diazotized 2-aminothiazoles and 2-aminobenzothiazoles in nitrosyl sulphuric acid. The dyes may exist in two tautomeric forms, namely the azohydroxypyridone form **A** and the diketohydrazone form **B**. The deprotonation of the two tautomers leads to a common anion **C**, as shown in Scheme 1.

The infrared spectra of all the compounds (in KBr) showed two intense carbonyl bands at 1700 and 1600 $cm^{-1}$; intensities of the two bands were very similar, and the latter band is related to intramolecularly hydrogen-bonded carbonyl. It was therefore assigned to the diketohydrazone form **B**. In the infrared spectra of the compounds in $CHCl_3$, two carbonyl bands were also observed, with the 1600 $cm^{-1}$ band having lower intensity. This suggests that the dyes exist in the hydrazone form in the solid state and

**TABLE 2**
Elemental Analysis of Compounds **1** and **2**

| *Compound no.* | *Molecular formula* | *C (%)* |  | *H (%)* |  | *N (%)* |  | *S (%)* |  | *Melting point (°C)* |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  | *Calcd.* | *Found* | *Calcd.* | *Found* | *Calcd.* | *Found* | *Calcd.* | *Found* |  |
| **1a** | $C_{14}H_{15}N_5O_2S$ | 52·99 | 53·21 | 4·73 | 4·77 | 22·08 | 22·16 | 10·09 | 9·98 | 212–213 |
| **1b** | $C_{14}H_{14}N_6O_4S$ | 46·41 | 46·72 | 3·87 | 3·91 | 23·20 | 23·26 | 8·84 | 8·75 | 179–180 |
| **2a** | $C_{18}H_{17}N_5O_2S$ | 58·85 | 58·52 | 4·63 | 4·55 | 19·07 | 18·76 | 8·72 | 8·68 | 270–271 |
| **2b** | $C_{18}H_{16}N_6O_4S$ | 52·43 | 53·12 | 3·88 | 3·91 | 20·39 | 20·47 | 7·77 | 7·65 | 228–230 |
| **2c** | $C_{19}H_{19}N_5O_3S$ | 57·43 | 56·43 | 4·78 | 4·77 | 17·63 | 17·35 | 8·06 | 8·02 | 265–267 |



**Scheme 1**

predominantly in the hydrazone form in $CHCl_3$. These conclusions are in accord with those of Cee *et al.*[7] and Cheng *et al.*[8]

Visible absorption maxima of the thiazolylazopyridones **1a** and **1b** and benzothiazolylazopyridones **2a-c** in various solvents are given in Table 3, and the spectra for **1b** in Fig. 1. The visible absorption spectra of the dyes were found to exhibit a strong solvent dependence which did not show a regular variation with the dielectric constants of the solvent. It was observed that although in glacial acetic acid, chloroform, ethyl acetate, acetonitrile and acetone the absorption spectra of the dyes did not change significantly, $\lambda_{max}$ of the dyes shifted considerably in methanol, DMF and DMSO (e.g. dye **1b** $\lambda_{max}$ is 430 nm in $CHCl_3$ and 570 nm in DMSO). The absorption maxima of the dyes also showed bathochromic shifts when a small amount of piperidine was added to dye solutions in $CHCl_3$, ethyl acetate, acetonitrile and acetone. A typical example is shown in Fig. 2.

In Raman spectroscopic studies of arylazonaphthols, it was concluded that the hydrazone form is converted to the azo anion form in basic media.[9,10] Stoyanov and Antonov also reached the same conclusion with quantum chemical calculations of phenylazopyrazolone dyes.[11] Peng *et*

TABLE 3
Influence of Solvent on Absorption Maxima ($\lambda_{max}$, nm)

| *Dye* | *Acetic acid* | *Chloroform* | *Ethyl acetate* | *Acetonitrile* | *Acetone* | *Methanol* | *DMF* | *DMSO* |
|---|---|---|---|---|---|---|---|---|
| **1a** | 423 | 430 | 425 | 429 | 425 | 430 | 436 | 435 |
| **1b** | 426 | 430 | 427 | 430 | 429 | 535 | 568 | 570 |
| **2a** | 426 | 430 | 427 | 430 | 426 | 465 | 449 | 449 |
| **2b** | 418 | 427 | 419 | 426 | 419 | 495 | 528 | 528 |
| **2c** | 455 | 452 | 455 | 457 | 455 | 479 | 481 | 484 |

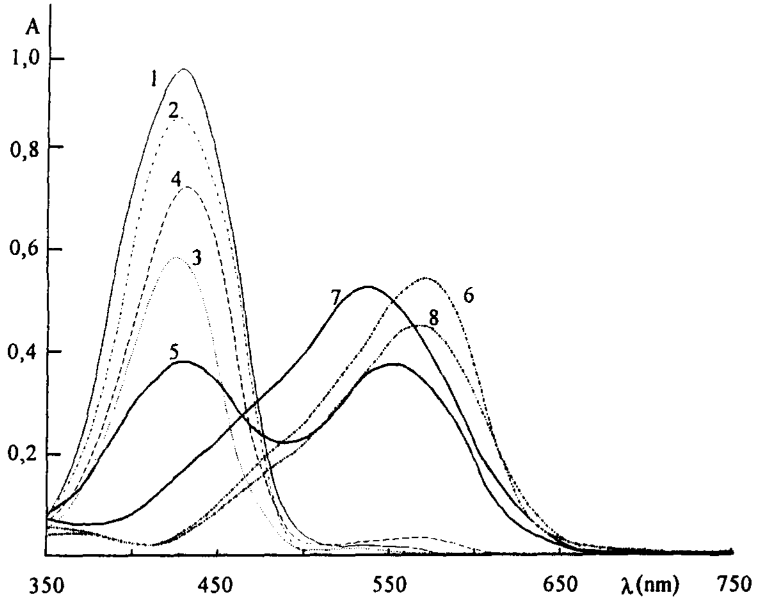


**Fig. 1.** Absorption spectra of dye **1b** in different solvents: 1, chloroform; 2, ethyl acetate; 3, acetic acid; 4, acetone; 5, acetonitrile; 6, DMSO; 7, methanol; 8, DMF.

*al.*[3] reported the same results for N-alkyl derivatives of arylazopyridones from $^{13}C$ chemical shift displacements at different pH in DMSO–water solutions. For the hetarylazopyridones, the absorption curves in methanol showed hypsochromic shifts when 0·1 M HCl was added, $\lambda_{max}$ values being the same as those observed in acetic acid. In contrast, addition of a small amount of piperidine or 0·1 M KOH to the methanol solutions of dyes caused no significant change in the spectra (Table 4). This indicates that the thiazolylazopyridones **1a** and **1b** and benzothiazolylazopyridones **2a** and **2b** are in a dissociated state in methanol, DMF and DMSO. These results are in agreement with those obtained for thiadiazolylazopyridones.[12] We therefore assigned the structures of the dyes prepared to the hydrazone form in acidic medium and to the common anion form in basic medium. The results show that hydrazone–common anion equilibria exist in solutions of hetarylazopyridones and that they could be ionized even in proton accepting solvents.

As shown in Table 3, while introduction of strongly acceptor nitro groups into both the thiazole (**1a**; R=H) and benzothiazole (**2a**; R=H) series results in large bathochromic shifts in methanol, DMF and DMSO (for dye **1b**, $\Delta\lambda$ = 135 nm relative to dye **1a**; for dye **2b** $\Delta\lambda$ = 79 nm relative to dye **2a**, for spectra in DMSO), it produces minimal hypsochromic shifts in other solvents (for dye **1b** $\Delta\lambda$ = 0 nm relative to dye **1a**; for dye **2b**

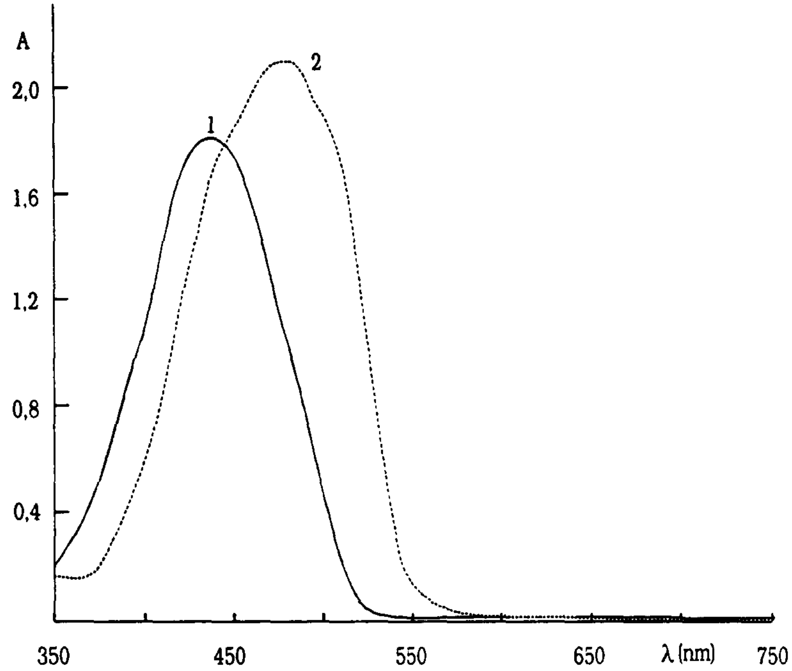


**Fig. 2.** Absorption spectra of dye **2a**: 1, in $CHCl_3$; 2, in $CHCl_3$ + piperidine.

$\Delta\lambda$ = 3, relative to dye **2a** in $CHCl_3$). This indicates that the nitro group facilitates the dissociation of hetarylazopyridone dyes and has little effect on the colour of the hydrazone form. In contrast, introduction of the donor methoxy group into the 6-position of the benzothiazole ring (dye **2c**) results in a marked bathochromic shift in the hydrazone form ($\Delta\lambda$ = 22 nm in $CHCl_3$ relative to **2a**).

TABLE 4

Absorption Maxima of Dyes **1** and **2** in Acidic and Basic Solutions

| *Dye* | $\lambda_{max}$ *(nm)* | | | | | | |
|---|---|---|---|---|---|---|---|
| | $CH_3COOH$ | $CH_3OH$ | $CH_3OH$ + piperidine | $CH_3OH$ + KOH | $CH_3OH$ + HCl | $CHCl_3$ | $CHCl_3$ + piperidine |
| **1a** | 423 | 430<br>465s[a] | 430<br>465s[a] | 429<br>465s[a] | 424 | 430 | 469 |
| **1b** | 426 | 535 | 531 | 532 | 427 | 430 | 542 |
| **2a** | 426 | 465 | 465 | 468 | 428 | 430 | 470 |
| **2b** | 418 | 495 | 497 | 495 | 418 | 427 | 505 |
| **2c** | 455 | 479 | 480 | 480 | 456 | 452 | 488 |

[a] Shoulder.

Spectra of the dyes in $CHCl_3$ and DMSO were also examined in the temperature range 25–80°C and $\lambda_{max}$ values of the dyes did not change significantly. This result supports the dissociation equilibria of hetarylazopyridones in neutral polar solvents (which do not involve change of energy) because it has been shown that azo–hydrazone equilibria are affected by temperature.[13]

## ACKNOWLEDGEMENTS

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