

## Effect of substituents on the absorption spectra and $pK$ values of some azo dyes derived from thiobarbituric acid

MINATI KUANAR and B K MISHRA\*

Department of Chemistry, Sambalpur University, Jyoti Vihar 768 019, India

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**Abstract.** A series of azo dyes from aromatic diazonium salts and thiobarbituric acid have been synthesised and their UV-Vis spectra have been recorded in neutral media and at two extreme  $pH$  values. The absorption maxima have been correlated with Swain–Lupton's  $F$  and  $R$  parameters using Williams–Norrington's weightage factors. The  $pK$  values of the dyes have also been determined and are highly predictable using Williams–Norrington's model.

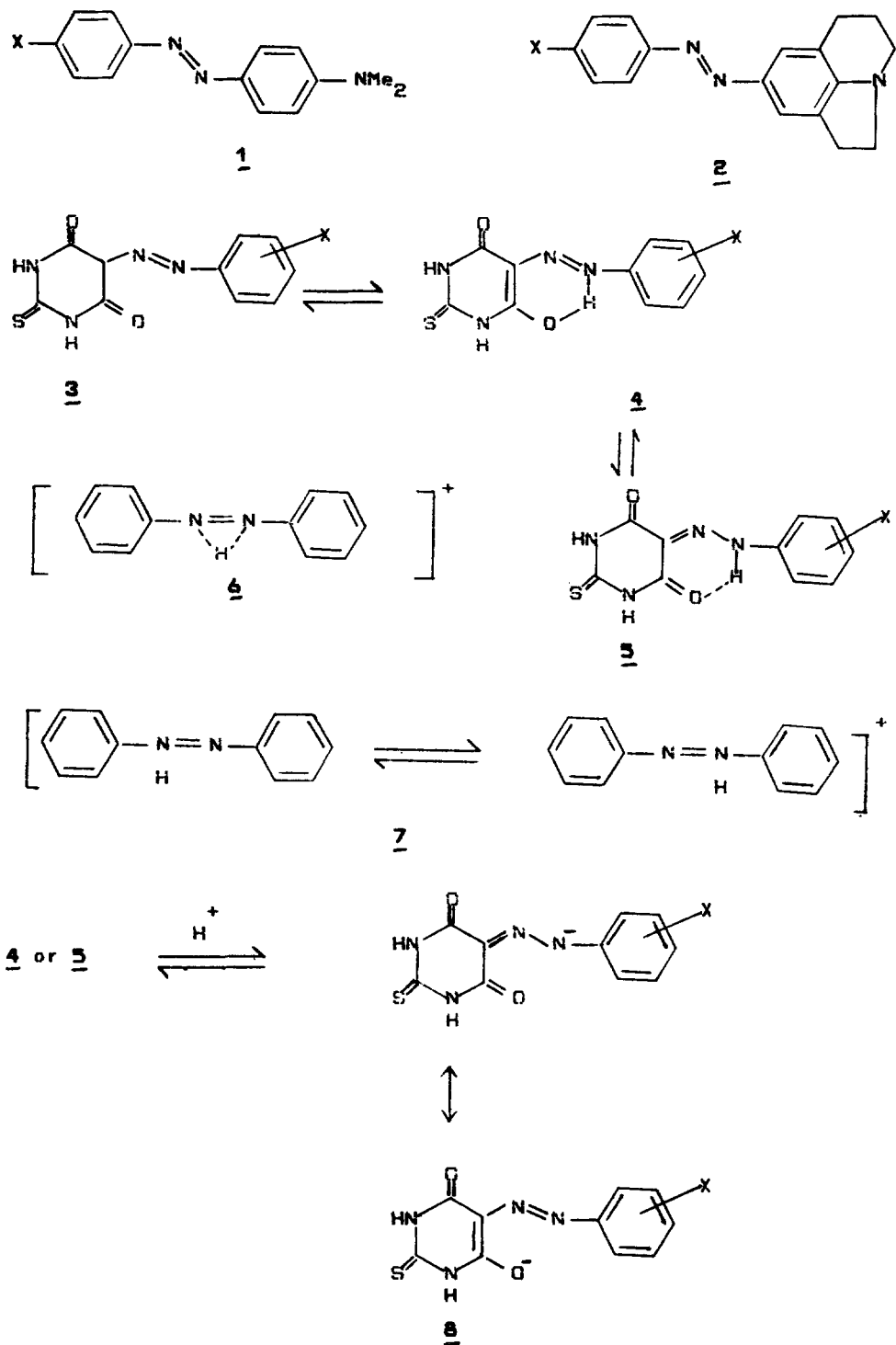
**Keywords.** Azo dyes; substituent effect; correlation analysis; dissociation constant.

### 1. Introduction

Azo dyes have an important place in the family of dyes due to the fact that they comprise practically every shade from yellow to black. Their applications include acid dyes for wool and polyamides, basic dyes for acrylic fibres, direct dyes for cotton and viscous rayon, disperse dyes for polyesters, and reactive dyes for cellulose (Stead 1970). These dyes are also used in the dyeing of paper and leather. In general, azo dyes are characterised by the presence of one or more azo groups, i.e.  $-N=N-$ , which form bridges between two organic residues.

Azobenzenes have significant substituent effect on absorption maxima. Both donor and acceptor substituents produce red shift of the absorption band of the parent compound (Tomasick 1970). However, stronger donor substituents like hydroxy, mercapto or amino groups give rise to a stronger bathochromic shift than acceptor substituents. Because both donor and acceptor substituents show isodirectional shift, the substituent parameters like Swain–Lupton's  $F$  and  $R$  parameters (Swain and Lupton 1968) cannot normally be applicable to these systems. But the absorption maxima of some protonated aminoazobenzenes (1) and (2) (Yagupol'ski and Gandel'sman 1965; Hallas *et al* 1974) and the spectral shifts in relation to the unprotonated parent compounds indicate a similar trend of electron-donation and -withdrawal in the substituted compounds. Gustavo *et al* (1991) have studied the acid–base behaviour of some substituted azo dyes in aqueous DMF. However, they have not studied the substituent effect on absorption maxima values. In the present report an attempt has been made to study the effect of substituents on the absorption maximum and  $pK$  values of some aryldiazothiobarbituric acids (3a–i) by using Williams–Norrington's (WN) model (Williams and Norrington 1976, (1) below). Recently we have reported the application of the WN model to explain the influence of substituents on the absorption maxima of

\* For correspondence



Scheme 1

arylidine thiobarbituric acid derivatives (Kuanar and Mishra 1995).

$$P = \alpha_i f_j F_k + \beta_i r_j R_k + P_{ijk}^0 \quad (1)$$

In (1),  $P$  is the dependent parameter;  $F_k$  and  $R_k$  are the position-independent Swain-Lupton field and resonance parameters of the substituent,  $k$ ;  $f_j$  and  $r_j$  are the WN-weightage factors ( $f_o = 1.248$ ,  $f_m = 0.980$ ,  $f_p = r_p = 1$ ,  $r_o = 0.863$  and  $r_m = 0.347$ ) for the substituents at ortho, meta or para position,  $j$ ;  $\alpha_i$  and  $\beta_i$  are the sensitivities of the field and resonance contribution in a particular system,  $i$ , respectively.

## 2. Experimental

### 2.1 Materials

Melting points are uncorrected. Carbon and hydrogen analyses were carried out on an MLW-GDR microanalyser. Sulphur was estimated by the standard procedure (Weiss 1970). The analytical data of the synthesised compounds are given in table 1.

### 2.2 Synthesis of 5-phenyldiazo-2-thiobarbituric acid

Aniline (0.93 g, 0.01 mole) was dissolved in water (20 ml) containing concentrated hydrochloric acid (4 ml) and was kept in ice-salt mixture to maintain the temperature below 5°C. To this mixture, an almost equally cooled 5% solution of sodium nitrite (14 ml) was added with stirring in an ice bath. This diazotised aniline solution was then

**Table 1.** Characterisation data for (X-substituted phenyl) 2-thiobarbituric acid (3).

| Structure | Substituent X             | Yield (%) | M.P. (°C) | Found (Calc.) % |              |                |
|-----------|---------------------------|-----------|-----------|-----------------|--------------|----------------|
|           |                           |           |           | C               | H            | S              |
| <u>3a</u> | H                         | 50        | > 260     | 48.6<br>(48.4)  | 3.2<br>(3.2) | 12.3<br>(12.9) |
| <u>3b</u> | <i>p</i> -OMe             | 72        | > 260     | 47.6<br>(47.5)  | 3.6<br>(3.5) | 11.7<br>(11.5) |
| <u>3c</u> | <i>p</i> -Cl              | 70        | 248       | 42.3<br>(42.5)  | 2.8<br>(2.5) | 10.8<br>(11.3) |
| <u>3d</u> | <i>p</i> -NO <sub>2</sub> | 57        | 250       | 40.7<br>(41.0)  | 2.4<br>(2.4) | 10.7<br>(10.7) |
| <u>3e</u> | <i>p</i> -Me              | 68        | 262       | 50.4<br>(50.4)  | 3.7<br>(3.8) | 11.8<br>(12.2) |
| <u>3f</u> | <i>m</i> -OMe             | 47        | 256       | 47.3<br>(47.5)  | 3.7<br>(3.5) | 11.4<br>(11.5) |
| <u>3g</u> | <i>m</i> -Me              | 44        | 260       | 50.3<br>(50.4)  | 3.6<br>(3.8) | 12.1<br>(12.2) |
| <u>3h</u> | <i>o</i> -NO <sub>2</sub> | 25        | 234       | 40.6<br>(41.0)  | 2.4<br>(2.4) | 10.8<br>(10.7) |
| <u>3i</u> | <i>o</i> -Cl              | 67        | > 260     | 42.8<br>(42.5)  | 2.3<br>(2.5) | 11.2<br>(11.3) |

added to thiobarbituric acid (1.44 gm, 0.01 mole) in 25 ml of 2 N sodium hydroxide dropwise with constant stirring at the same temperature. A purple-coloured compound soon formed which was isolated in an acidic medium maintained by slow dropwise addition of precooled 2N hydrochloric acid. The solid thus separated out was filtered off, washed with cold water, dried, and crystallised from methanol, m.p. 260°C, yield 81%, IR (KBr) ( $\text{cm}^{-1}$ ) 3260, 2890, 1705, 1600, 1500, 1460, 1430. The other azo dyes were similarly synthesised.

Dioxane was purified to spectroscopic grade by using the technique of Eigenburger (1931). Triple-distilled water was used for preparing the solution of the dyes (3a-j) in water-dioxane mixture (85:15v/v).

Methanol (AR grade) was used to prepare stock solutions of the dyes so that the experimental concentrations were maintained at  $2.5 \times 10^{-5}$  M. A buffer solution was prepared from a mixture of solution A (6.043 g of citric acid, 3.450 g of boric acid, 19 ml of N-phosphoric acid and 343 ml of N-sodium hydroxide, and the mixture diluted to 1000 ml) and solution B (0.01N HCl). Different volumes of solution A and solution B, on mixing, cover the pH range from 2 to 13 (Mishra *et al* 1988). To obtain pH 1, 0.1N HCl was used.

### 2.3 Methods

A Hitachi 200-20 UV-Vis spectrophotometer attached to a thermostatic cell holder was used to record the spectra. Water was circulated from a cryostat maintaining water temperature at  $\pm 0.1^\circ\text{C}$  of that required. The stock solution was diluted in different buffers (the experimental  $[\text{dye}] = 2.5 \times 10^{-5}$  M) and electronic spectra at different visible regions were recorded. By analysing the spectra at various pH values the analytical wavelengths have been found to be the  $\lambda_{\text{max}}$  in each case. A representative scanning of spectra at different pH values is shown in figure 1. The pK values have

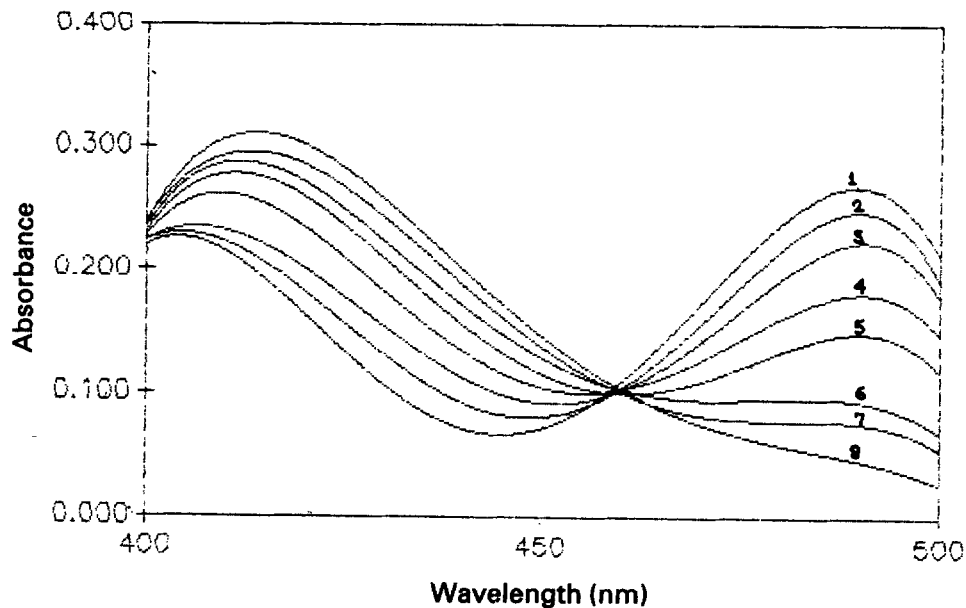


Figure 1. Electronic absorption spectra of 3d in buffer solutions at pH: 1, 11.85; 2, 11.64; 3, 11.41; 4, 11.28; 5, 11.07; 6, 10.01; 7, 10.62; 8, 10.53.

**Table 2.** Absorption maxima of **3** in dioxane–water medium under neutral, acidic (*pH* = 1) and alkaline (*pH* = 13) conditions and *pK* values in dioxane–water medium.

| Structure | Absorption maxima (nm) dioxane–water | Wavelength in nm at <i>pH</i> = 1 (CaCl) <sup>a</sup> | Obs. <i>pK</i> <sub>1</sub> (CaCl) <sup>b</sup> | Wavelength in nm at <i>pH</i> = 13 (CaCl) <sup>c</sup> | Obs. <i>pK</i> <sub>2</sub> (CaCl) <sup>d</sup> |
|-----------|--------------------------------------|---|---|--|---|
| <b>3a</b> | 415                                  | 435<br>(433)  | 5.91<br>(5.92)                                  | 390<br>(399)   | 10.98<br>(10.95)                                |
| <b>3b</b> | 438                                  | 466<br>(479)  | 6.02<br>(6.04)                                  | 360<br>(340)   | 10.64<br>(10.55)                                |
| <b>3c</b> | 418                                  | 450<br>(424)  | 5.90<br>(5.92)                                  | 370<br>(410)   | 10.89<br>(10.89)                                |
| <b>3d</b> | 418                                  | 365<br>(366.2)  | 5.80<br>(5.80)                                  | 490<br>(484)   | 11.24<br>(11.22)                                |
| <b>3e</b> | 416                                  | 435<br>(453)  | 5.98<br>(5.97)                                  | 390<br>(373.3)   | 10.82<br>(10.82)                                |
| <b>3f</b> | 418                                  | 430<br>(438)  | 6.01<br>(5.95)                                  | 395<br>(393)   | 10.62<br>(10.85)                                |
| <b>3g</b> | 419                                  | 435<br>(441)  | 5.92<br>(5.94)                                  | 390<br>(388.2)   | 10.96<br>(10.90)                                |
| <b>3h</b> | 422                                  | 365<br>(379)  | 5.76<br>(5.78)                                  | 485<br>(464.2)   | 11.26<br>(11.24)                                |
| <b>3i</b> | 414                                  | 450<br>(437.4)  | 5.92<br>(5.90)                                  | 370<br>(389.1)   | 10.93<br>(10.93)                                |

Using <sup>a</sup>(6), <sup>b</sup>(8), <sup>c</sup>(7), <sup>d</sup>(9).

been determined by using the Henderson equation (Albert and Serjeant 1984) and are given in table 2. Multiple regression analysis was made using an SAS software package.

### 3. Results and discussion

#### 3.1 Quantitative structure–spectra relationship

The absorption maxima of **3a–i** in dioxane–water medium are in the range 415–438 nm. Compounds with both electron-donating and electron-withdrawing groups have higher  $\lambda_{\max}$  values than unprotonated ones and thus  $\lambda_{\max}$  values do not correlate well with the Swain–Lupton and WN parameters. When fitted to the WN model (1) the resultant equation, (2), shows a poor regression coefficient value ( $r = 0.72$ ).

$$\lambda_{\max}^{\text{Dioxane-Water}} = 414.27 + 5.13f_j F_k - 28.80r_j R_k \quad (2)$$

$$n = 9, r = 0.72, s = 5.81, F_s = 3.19,$$

where  $n$  is the number of compounds,  $r$  is the regression coefficient,  $s$  is the standard deviation, and  $F_s$  is the statistical  $F$  test value.

But when absorption maxima of protonated species of **3** at  $pH = 1$  have been fitted to the WN model, a better coefficient value of 0.91 is obtained,

$$\lambda_{\max}^{pH=1} = 426.19 - 24.83f_j F_k - 129.76r_j R_k, \quad (3)$$

$$n = 9, r = 0.91, s = 17.80, F_s = 13.49.$$

Equation (3) shows that the percentage of resonance contribution ( $100\alpha_i/\alpha_i + \beta_i = 80.4$ ) is much higher than that of field contribution ( $100\beta_i/\alpha_i + \beta_i = 19.6\%$ ) towards the absorption maxima. At  $pH = 1$  the absorption maxima are in the order:  $p\text{-OMe} > p\text{-Cl} > o\text{-Cl} > p\text{-Me} = H = m\text{-Me} > m\text{-OMe} > p\text{-NO}_2 = o\text{-NO}_2$  whereas at  $pH = 13$ , the order is  $p\text{-NO}_2 > o\text{-NO}_2 > m\text{-OMe} > H = p\text{-Me} = m\text{-Me} > p\text{-Cl} = o\text{-Cl} > p\text{-OMe}$ .

The regression equation (4) below shows the correlation of the substituent parameters with the absorption maxima of **3** at  $pH = 13$ . The regression coefficient is found to be 0.88 and the resonance and field contributions are 81.9% and 18.9% respectively.

$$\lambda_{\max}^{pH=13} = 400.71 + 36.73f_j F_k + 161.40r_j R_k, \quad (4)$$

$$n = 9, r = 0.88, s = 26.37, F_s = 13.57.$$

The incorporation of the steric parameter, steric density (SD) (Dash *et al* 1980), improves the regression coefficient values, (5)–(7). Values of absorption maxima calculated by using (6) and (7) are given in table 2.

$$\lambda_{\max}^{\text{Dioxane-Water}} = 413.98 + 7.82f_j F_k - 28.68r_j R_k - 1.98SD, \quad (5)$$

$$n = 9, r = 0.76, s = 5.97, F_s = 2.42$$

$$\lambda_{\max}^{pH=1} = 433.00 - 42.46f_j F_k - 127.05r_j R_k + 8.75SD, \quad (6)$$

$$n = 9, r = 0.94, s = 16.08, F_s = 12.75$$

$$\lambda_{\max}^{pH=13} = 398.92 + 53.80f_j F_k + 162.16r_j R_k - 12.61SD, \quad (7)$$

$$n = 9, r = 0.91, s = 25.29, F_s = 8.20.$$

The dye under study (**3**) may assume different structures due to ease in keto enol tautomerization (**4**) and hydrogen migration (**5**). The protonation of the dye in acid solution occurs at the nitrogen atoms of the diazo group and deprotonation in alkaline medium occurs at the hydroxy group. From the study of protonation equilibria, Yeh and Jaffe (1959) suggested the formation of a symmetrical diazonium cation, **6**, but later experimental results supported the classical structure, **7**, for the protonated azobenzene. X-ray photoelectron spectroscopy has also supported the latter structure (Haselbach 1973).

The dye has an intramolecular hydrogen bonded structure (**4**) where N-2 is involved in hydrogen bonding which can facilitate migration of hydrogen to assume the hydrazone structure, **5**.

Fabian (1980) has reported that protonation of 1-phenyl azo 2-naphthol in its hydrazone structure causes a bathochromic shift. The protonated dyes in the present study are found to have  $\lambda_{\max}$  values in the range of 360–485 nm. The compounds with nitro groups experience large hypsochromic shifts ( $\Delta\lambda_{\max} = 51\text{--}57$  nm) while compounds with other substituents experience bathochromic shifts ( $\Delta\lambda_{\max} = 16\text{--}36$  nm). This variation may be attributed to the electron-withdrawing tendency at both ends of the chromophoric group of the former set of compounds.

In alkaline medium deprotonation occurs to give an anionic dye (8). Deprotonation occurs from the 1-phenylazo 4-naphthol compound leading to the formation of the corresponding anionic derivative with a bathochromic shift of 93 nm from that of parent dye (Griffith 1972), whereas when the protonation is on the hydrazone structure the shift is only 22 nm. In the present study the deprotonation of 4 or 5 leads to the formation of an anion 8 which experiences a bathochromic shift of 63–72 nm for nitro-substituted compounds, while the parent compound shows a hypsochromic shift of 23–78 nm. In the former case the electron flow is from a strong auxochrome ( $-O^-$ ) to an electron-acceptor group while in the latter case electron-donating groups are present at both ends of the chromophoric group.

The variance of  $\lambda_{\max}$  values of nitro-substituted dyes, due to substituent position in the benzene nucleus, is interesting. Generally, ortho-substituted dyes suffer a hypsochromic shift when compared to para-substituted dyes (Bridgeman and Peters 1970; Griffith and Roozpeikar 1976). In dioxane–water medium *o*-nitro substituted dyes have higher  $\lambda_{\max}$  values than the *p*-nitro substituted dyes. This deviation may be attributed to the intramolecular hydrogen bonding between the nitro group and hydrogen of hydrazone or hydroxy unit in *o*-substituted dyes. This type of hydrogen bonding does not prevail in deprotonated dyes and hence the order of  $\lambda_{\max}$  values is found to be reversed in media of high pH values. Under acidic conditions, the  $\lambda_{\max}$  values of both the compounds are about the same.

### 3.2 Quantitative structure–property relationship

The  $pK$  values of the dyes under study are in the range 5.76–6.02 ( $pK_1$  due to protonation) and 10.62–11.26 ( $pK_2$  due to dissociation). Table 2 shows that compounds with electron-donating groups have higher  $pK_1$  values than compounds with electron-withdrawing groups. When the WN model is used to derive a correlation between substituent parameters and  $pK_1$ , (8) is found to have high predictability,

$$pK_1 = 5.29 - 0.07f_j F_k - 0.30r_j R_k, \quad (8)$$

$$n = 9, r = 0.94, s = 0.03, F_s = 23.03.$$

The regression model obtained was at a confidence level of 99%. The resonance contribution is 81.2% which is four times more than the field contribution. This finding is explicable on the basis of the structure where the protonation site is influenced by resonance. The incorporation of the steric parameter does not improve the correlation coefficient.

Similarly, analyses of dissociation constant values ( $pK_2$ ) reveal that electron-donating substituents decrease the dissociation constants while electron-withdrawing groups increase them. In this case also the ortho effect could not be felt which may be due to the presence of a negative charge on the oxygen atom which is more probable than on a nitrogen atom.

The WN-model was applied to obtain a regression equation

$$pK_2 = 10.95 + 0.12f_j F_k + 0.89r_j R_k, \quad (9)$$

$$n = 9, r = 0.92, s = 0.10, F_s = 16.16.$$

The regression model is at 95% confidence level. The percent contribution of resonance is seven times greater than the field effect.

Thus it is seen that the WN-model can explain both spectral and dissociation data quantitatively in the substituted azo dyes under study.

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