# Synthesis and tautomeric structure of 3,6-bis(arylazo)pyrazolo [1,5-*a*]pyrimidine-5,7(4*H*,6*H*)-diones

**Ahmad S. Shawali*, Mosselhi A. N. Mosselhi, Thoraya A. Farghaly, Mohamed R. Shehata and Nagla M. Tawfik**

*Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt*

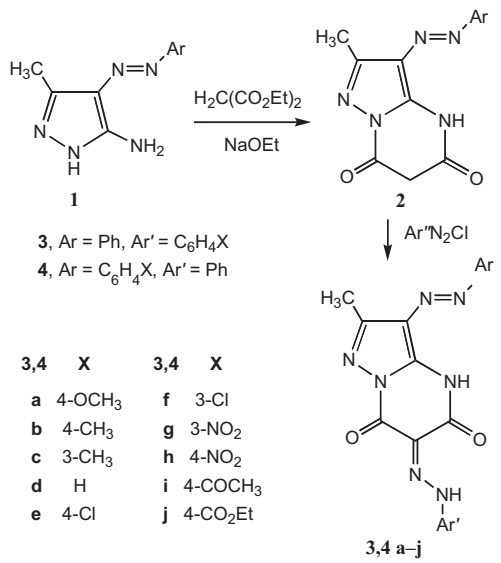
Two series of 3,6-*bis*(arylazo)pyrazolo[1,5-*a*]pyrimidine-5,7-diones were prepared, and their acid dissociation constant $pK_a$s were determined and correlated with the Hammett equation. The results of these correlations, together with the spectroscopic data, indicated that the title compounds exist predominantly in the 3-arylazo-6-arylhydrazonopyrazolo[1,5-*a*]pyrimidine-5,7-dione tautomeric form, both in the solid and solution phases.

**Keywords:** azo-hydrazone tautomerism, pyrazoles, fused pyrazoles, pyrimidines, Hammett equation

A literature search revealed that many arylazoheterocycles are evaluated and patented for use in various sectors of industry, including hair dyeing, thermal transfer printing, nonlinear optics, disperse dyes, pigments, dyeing and printing polyesters, and ink-jet inks.[1] In the light of these applications, and as part of our comprehensive programme for the synthesis and elucidation of the tautomeric structures of bis(arylazo) heterocycles,[2-4] we report here the synthesis of two new series of bis-azo dyes which have not been reported previously. Our interest in such azo derivatives is to elucidate their tautomeric structure prior to exploring their utility. This is because such dyes can exist in one or other of the seven tautomeric forms **A–G** depicted in Fig. 1. The authors of an earlier report[5] assigned the tautomeric form **E** to three such dyes without providing spectroscopic evidence for their assignment. A knowledge of the precise tautomeric form(s) of azo dyes in solution and in the solid phase is an important factor in the industrial and biological applications of azo dyes. Furthermore, investigation of azo-hydrazone tautomerism is of interest from a practical and theoretical point of view.

## Results and discussion

The synthetic approach to the target azo dyes is outlined in Scheme 1. The starting 3-arylazo-2-methylpyrazolo[1,5-*a*] pyrimidine-5,7(4*H*,6*H*)-diones **2** were prepared by reaction of diethyl malonate with the 5-amino-4-arylazo-3-methylpyrazoles **1** as previously described.[5,6] Coupling of **2d** with diazotised anilines in aqueous ethanol in the presence of sodium acetate yielded the respective bis-arylazo derivatives **3a–j**. Similar coupling of diazotised aniline with each of **2a–i** under the same conditions afforded the bis-arylazo derivatives **4a–j** (Scheme 1).




**Scheme 1**

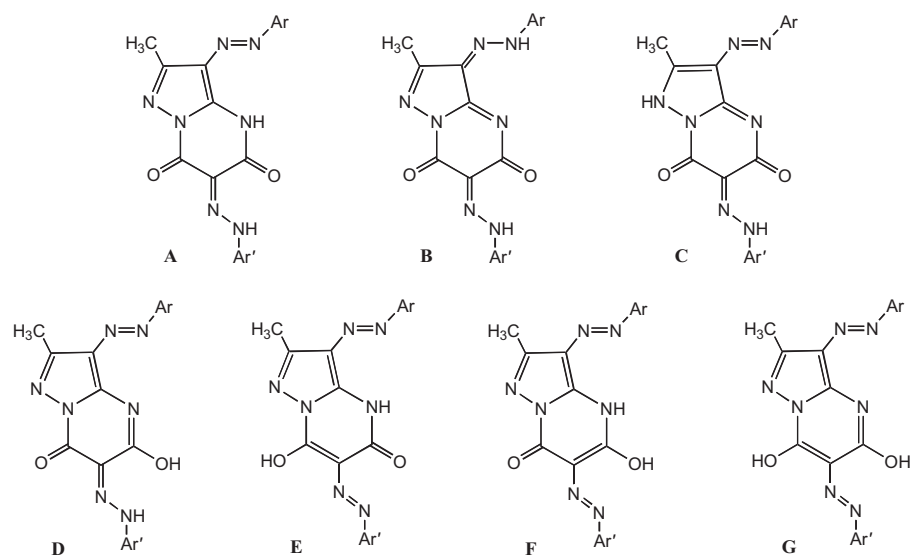



**Fig. 1** Prototropic tautomerism in the 3-(arylazo)-6-(arylhydrazono)pyrazolo[1,5-*a*]pyrimidine-5,7-diones.

* Correspondent. E-mail: as_shawali@mail.com

**Table 1** Electronic absorption spectra of compounds **3** in dioxan–water and their acid dissociation constants[a]

| Compd | $\lambda_{max}$ (log ε) | p$K_1$ | p$K_2$ | $\sigma_X^-$ |
|---|---|---|---|---|
| 3a | 437 (4.85), 327 (4.39) | 6.63 | 9.65 | -0.27 |
| 3b | 436 (4.82), 327 (4.39) | 6.62 | 9.43 | -0.17 |
| 3c | 412 (5.02), 387 (5.02) | 6.59 | 9.20 | -0.07 |
| 3d | 424 (4.95), 340 (4.54)[b] | 6.57 | 9.08 | 0.00 |
| 3e | 424 (4.37), 330 (4.37) | 6.51 | 8.55 | 0.23 |
| 3f | 417 (4.76), 326 (4.56) | 6.46 | 8.18 | 0.37 |
| 3g | 407 (4.67), 337 (4.50) | 6.36 | 7.43 | 0.71 |
| 3h | 414 (4.75), 320 (4.54) | 6.18 | 6.10 | 1.28 |
| 3i | 423 (4.71), 336 (4.52) | 6.36 | 7.43 | 0.68 |
| 3j | 412 (4.89), 329 (4.74) | 6.32 | 7.06 | 0.84 |

[a]In dioxan-water (1:1 v/v) at 25 °C, μ = 0.10 and standard deviation s = ± 0.03-0.05.
[b]Solvent $\lambda_{max}$ (log ε): acetic acid 429 (4.75), 329 (4.37); ethanol 424 (4.70), 330 (4.22); chloroform 440 (4.70), 340 (4.30); petroleum ether 425 (4.76), 335 (4.37).

**Table 2** Electronic absorption spectra of compounds **4** in dioxan–water and their acid dissociation constants[a]

| Compd | $\lambda_{max}$ (log ε) | p$K_1$ | p$K_2$ | $\sigma_X^-$ |
|---|---|---|---|---|
| 4a | 431 (4.92), 355 (4.64) | 6.91 | 9.15 | -0.27 |
| 4b | 424 (4.91), 339 (4.56) | 6.79 | 9.12 | -0.17 |
| 4d | 424 (4.95), 340 (4.54) | 6.57 | 9.08 | 0.00 |
| 4e | 419 (4.71), 329 (4.44) | 6.28 | 9.01 | 0.23 |
| 4f | 424 (4.65), 346 (4.73) | 6.07 | 8.97 | 0.37 |
| 4g | 420 (4.77), 377 (4.83) | 5.63 | 8.87 | 0.71 |
| 4h | 422 (4.70), 383 (4.65) | 4.92 | 8.71 | 1.28 |
| 4i | 444 (4.65), 339 (4.53) | 5.71 | 8.88 | 0.68 |

[a]In dioxan–water (1:1 v/v) at 25 °C, μ = 0.10 and standard deviation s = ± 0.03–0.05.

The structures of the isolated products **3** and **4** were established by their spectroscopic (IR, $^1$H NMR and MS) data and elemental analyses (see Experimental). Each can exist in one or other of the seven tautomeric structures **A-G** (Fig. 1). To ascertain the actual tautomeric structure(s) of such products, their IR, $^1$H NMR and UV spectra were examined. Their IR spectra reveal, in each case, two C=O vibration bands in the regions 1725–1710 and 1663–1656 cm$^{-1}$. In addition, their spectra showed NH bands in the regions 3317–3216 cm$^{-1}$ (see Experimental). Such data, while consistent with one of the three tautomeric forms **A–C**, exclude the tautomeric forms **D–G**. The structure **C** was discarded on the basis of the $^1$H NMR spectral data. Thus, their $^1$H NMR spectra in DMSO showed, in each case, two characteristic signals assignable to hydrazone and amide protons in the regions δ 15.32–13.65 and 12.45–12.00, respectively. Furthermore, their electronic absorption spectra in dioxan display, in each case, two absorption bands in the regions 444–407 and 387–302 nm (Tables 1 and 2). The spectra of the unsubstituted derivative **3d,** taken as typical example of the two series prepared, in different solvents of different polarity, showed little, if any, change (Table 1, footnote b). Such spectral data collectively indicate that the products **3** and **4** exist in one tautomeric form, namely the azo-hydrazone form **A**.

To provide further evidence for the assignment of the tautomeric structure **A** to compounds **3** and **4,** their acid dissociation constants were determined and their correlation with Hammett substituent constants were examined.[3,7-10] The acid dissociation constants for the two series **3a–j** and **4a–i** were determined potentiometrically at 25 ± 0.1 °C in 50% dioxan-water mixture (v/v). In all determinations, the ionic strength was kept constant at 0.1 M. From the pH-titrant volume data, the acid dissociation constants of the compounds **3** and **4** were calculated and the results are summarised in Tables 1 and 2. These results show that each of the studied dyes behaves as a dibasic acid ($H_2A$) since each dye has two acidity constants p$K_1$ and p$K_2$. For series **3**, the higher acidity constant $K_1$ was found to be independent of the nature of the substituent in the arylazo group at position 3, whereas the lower acidity constant $K_2$ is affected by such substituents (Table 1). In contrast to this, for series **4**, the higher acidity constant $K_1$ was found to be dependent on the nature of the substituent in the arylazo group, whereas the lower acidity constant $K_2$ is independent of such substituents. These findings seem consistent with the tautomeric structure **A** and indicate that $K_1$ and $K_2$ correspond to the deprotonation of the hydrazone NH and amide NH groups, respectively. This assignment is further supported by correlation of the pK values of each series with the Hammett equation ($pK_a = pK_0 - \rho \sigma_X^-$).[11] Thus, when the p$K_2$ values for the studied compounds **3** are plotted *versus* Hammett substituent constant $\sigma_X^-$, a linear correlation was obtained. The equation of the regression line obtained is:

$$pK_2\ (\mathbf{3}) = 9.05 - 2.297\ \sigma^-_x$$

with correlation coefficient $r^2 = 0.999$ and standard deviation s = ± 0.04. The p$K_1$ values for the other series **4** gave also a linear correlation with Hammett substituent constant $\sigma^-_x$ [11]. The equation of the regression line obtained is:

$$pK_1(\mathbf{4}) = 6.57 - 1.289\ \sigma^-_x$$

with correlation coefficient $r^2 = 0.999$ and standard deviation s = ± 0.02.

Such linear correlations and the values of the reaction constant ρ provide further evidence that both series of compounds **3** and **4** exist predominantly in the 4*H*-6-arylhydrazono-3-arylazo form **A** and exclude the tautomeric structure **B** (Fig. 1). This is because, if the structure **B** were the predominant form, it would be expected that both ρ values for the two series will be similar, and this is found not to be the case. Furthermore, the value of $\rho_2$ (2.297) found for series **3** is similar to that reported for ionisation of phenols (ρ = 2.67), anilinium ions (ρ = 2.77) [12-15] and typical arylhydrazones (ρ = 2.51)[12] in 50% ethanol–water. Also, the value of $\rho_1$ (1.289) found for series **4** is similar to that reported for ionisation of 2-arylazophenols (ρ = 1.223) in 50% ethanol–water.[13,16] The low value ($\rho_1$ = 1.289) seems to be due to the fact that the transmission factor for the bridge –N=N–C(8) =C(8a)- in form **A** is expected to be 0.32 as the transmission factor for –N=N– and –C=C– bridges were reported to be 0.69 and 0.47, respectively.[17]

In conclusion, both the spectral data and the observed linear correlation of the acid dissociation constants by the Hammett equation indicate collectively that the 4*H*-6-arylhydrazono-3-arylazo form **A** (Fig. 1) is the predominant tautomeric form for both compounds **3** and **4** in solid and solution phase.

## Experimental

Melting points were determined on a Gallenkamp apparatus. IR spectra were recorded in potassium bromide using Perkin Elmer FTIR 1650 and Pye-Unicam SP300 infrared spectrometers. $^1$H NMR spectra were recorded in deuterated chloroform or deuterated dimethyl sulfoxide using a Varian Gemini 300 NMR spectrometer. Mass spectra were recorded on GCMS-QP 1000 EX Shimadzu and GCMS 5988-A HP spectrometers. Electronic absorption spectra were recorded on a Perkin-Elmer Lamda 40 spectrophotometer. Elemental analyses were carried out at the Microanalytical Laboratory of Cairo University, Giza, Egypt.

2-Arylhydrazono-3-iminobutyronitriles were prepared by a literature method.[18]

*Preparation of 5-amino-4-arylazo-3-methylpyrazoles* (**1**): *General procedure*

A solution of 2-arylhydrazono-3-iminobutyronitrile (0.1 mol) and hydrazine hydrate (5.0 ml, 0.1 mol) in absolute ethanol (100 ml) was heated to reflux for 15 h, and then the solvent was evaporated under reduced pressure. The solid left was collected and recrystallised from the appropriate solvent to give the respective compound **1**. The physical constants of the compounds **1a–h** are given below.

*5-Amino-4-(4-methoxyphenylazo)-3-methylpyrazole* (**1a**): Yellow solid (19.9 g, 86%), m.p. 180–182 °C (EtOH) (Lit.[19] m.p. 187–188 °C). IR: $\nu_{max}$ 3467, 3355 cm$^{-1}$. NMR ($CDCl_3$) $\delta_H$ 2.35 (s, 3H, $CH_3$), 3.79 (s, 3H, $OCH_3$), 6.20 (s, 2H, $NH_2$), 6.98 (d, $J$ = 9 Hz, 2H, ArH), 7.64 (d, $J$ = 9 Hz, 2H, ArH), 11.60 (s, 1H, NH). MS *m/z* (%) 232 ($M^+$ + 1, 16), 231 ($M^+$, 100), 188 (11), 124 (70), 122 (11), 107 (13), 92 (27), 77 (26). Anal. Calcd. for $C_{11}H_{13}N_5O$ (231.26): C, 57.13; H, 5.67; N, 30.28. Found: C, 56.82; H, 5.43; N, 30.00%.

*5-Amino-3-methyl-4-(4-methylphenylazo)pyrazole* (**1b**): Yellow solid (17.4 g, 81%), m.p. 177 °C (EtOH) (Lit.[20] m.p. 178 °C).

*5-Amino-3-methyl-4-(phenylazo)pyrazole* (**1d**): Yellow solid (16.5 g, 82%), m.p. 164–166 °C (EtOH) (lit.[19] m.p. 165–166 °C).

*5-Amino-4-(4-chlorophenylazo)-3-methylpyrazole* (**1e**): Yellow solid (18.8 g, 80%), m.p. 180–182 °C (EtOH). IR: $\nu_{max}$ 3410, 3298 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.33 (s, 3H, $CH_3$), 6.35 (s, 2H, $NH_2$), 7.42 (d, $J$ = 9 Hz, 2H, ArH), 7.63 (d, $J$ = 9 Hz, 2H, ArH), 10.88 (s, 1H, NH). MS: *m/z* (%) 237 ($M^+$ + 2, 12), 236 ($M^+$ + 1, 5), 235 ($M^+$, 34), 139 (5), 124 (100), 113 (20), 111 (74), 95 (27), 76 (12). Anal. Calcd. for $C_{10}H_{10}ClN_5$ (235.68): C, 50.96; H, 4.28; N, 29.72. Found: C, 50.74; H, 4.01; N, 29.53%.

*5-Amino-4-(3-chlorophenylazo)-3-methylpyrazole* (**1f**): Yellow solid, (19.5 g, 83%), m.p. 168–170 °C (EtOH). IR: $\nu_{max}$ 3402, 3294 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.32 (s, 3H, $CH_3$), 6.42 (s, 2H, $NH_2$), 7.30–7.62 (m, 4H, ArH), 10.92 (s, 1H, NH). MS: *m/z* (%) 237 ($M^+$ + 2, 18), 236 ($M^+$ + 1, 4), 235 ($M^+$, 2), 224 (29), 222 (47), 167 (18), 152 (59), 150 (21), 139 (16), 129 (11), 125 (11), 111 (46), 93 (24), 76 (26). Anal. Calcd. for $C_{10}H_{10}ClN_5$ (235.68): C, 50.96; H, 4.28; N, 29.72. Found: C, 50.84; H, 4.18; N, 29.55%.

*5-Amino-3-methyl-4-(3-nitrophenylazo)-pyrazole* (**1g**): Yellow solid, (20.0 g, 82%), m.p. 210–212 °C (EtOH). IR: $\nu_{max}$ 3456, 3348 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.29 (s, 3H, $CH_3$), 6.50 (s, 2H, $NH_2$), 7.32–8.24 (m, 4H, ArH),11.02 (s, 1H, NH). MS: *m/z* (%) 247 ($M^+$ + 1, 4), 246 ($M^+$, 32), 172 (2), 124 (100), 122 (17), 92 (13), 76 (59). Anal. Calcd. for $C_{10}H_{10}N_6O_2$ (246.23): C, 48.78; H, 4.09; N, 34.13. Found: C, 48.33; H, 3.94; N, 34.05%.

*5-Amino-3-methyl-4-(4-nitrophenylazo)-pyrazole* (**1h**): Yellow solid (19.6 g, 80%), m.p. 150–152 °C (EtOH) (Lit[20]. m.p. 226–227 °C). IR: $\nu_{max}$ 3483, 3363 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.49 (s, 3H, $CH_3$), 5.80 (s, 2H, $NH_2$), 6.61 (d, $J$ = 8 Hz, 2H, ArH), 7.94 (d, $J$ = 8 Hz, 2H, ArH), 11.0 (s, 1H, NH). MS: *m/z* (%) 246 ($M^+$, 12), 245 (34), 124 (68), 105 (36), 91 (18), 77 (60). Anal. Calcd. for $C_{10}H_{10}N_6O_2$ (246.23): C, 48.78; H, 4.09; N, 34.13. Found: C, 48.62; H, 3.91; N, 33.84%.

*5-Amino-3-methyl-4-(4-acetylphenylazo)-pyrazole* (**1i**): Yellow solid (21.2 g, 87%), m.p. 218–220 °C (EtOH). IR: $\nu_{max}$ 3445, 3260, 1698 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.32 (s, 3H, $CH_3$), 2.49 (s, 3H, $CH_3$), 6.55 (s, 2H, $NH_2$), 7.21 (d, $J$ = 8 Hz, 2H, ArH), 7.51 (d, $J$ = 8 Hz, 2H, ArH), 11.32 (s, 1H, NH). MS: *m/z* (%) 245 ($M^+$ + 2, 1), 244 ($M^+$ + 1, 2), 243 ($M^+$, 7), 216 (12), 188 (12), 146 (3), 118 (13), 92 (45), 85 (14), 77 (19), 43 (100). Anal. Calcd. for $C_{12}H_{13}N_5O$ (243.27): C, 59.26; H, 5.35; N, 28.81. Found: C, 59.12; H, 5.40; N, 28.43%.

*Preparation of 3-arylazo-2-methylpyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-diones* (**2**): *general procedure*

To a suspension of the appropriate arylazopyrazole derivative **1** (5 mmol) in ethanol (20 ml), diethyl malonate (0.75 ml, 5 mmol) in ethanolic sodium ethoxide, prepared from sodium metal (0.58 g, 0.1 mole) and absolute ethanol (20 ml), was added. The mixture was refluxed for 30–50 hours. The solution was cooled and diluted with water, then acidified with conc. HCl. The precipitate that formed was filtered off and crystallised from the indicated solvent to give the respective compound **2**.

*3-(4-Methoxyphenylazo)-2-methylpyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**2a**): Orange solid (1.38 g, 92%), m.p. 240 °C (dioxan/MeOH). (lit.[5] m.p. 195 °C). IR: $\nu_{max}$ 3120, 1728, 1689 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.50 (s, 3H, $CH_3$), 3.84 (s, 3H, $OCH_3$), 5.11 (s, 2H, $CH_2$), 7.05 (d, $J$ = 9 Hz, 2H, ArH), 7.88 (d, $J$ = 9 Hz, 2H, ArH), 11.84 (s, 1H, NH). MS: *m/z* (%) 301 ($M^+$ + 2, 3), 300 ($M^+$ + 1, 20), 299 ($M^+$, 100), 203 (27), 192 (31), 188 (23), 164 (18), 122 (45), 107 (46), 92 (34), 77 (45). Anal. Calcd for $C_{14}H_{13}N_5O_3$ (299.29): C, 56.19; H, 4.35; N, 23.41. Found: C, 56.20; H, 4.00; N, 23.13%.

*2-Methyl-3-(4-methylphenylazo)pyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**2b**): Orange solid (1.26 g, 89%), m.p. 234–235 °C (dioxan). IR: $\nu_{max}$ 3246, 1700, 1660 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.37 (s, 3H, $CH_3$), 2.49 (s, 3H, $CH_3$), 5.15 (s, 2H, $CH_2$), 7.30 (d, $J$ = 8 Hz, 2H, ArH), 7.76 (d, $J$ = 8 Hz, 2H, ArH), 11.90 (s, 1H, NH); MS *m/z* (%) 285 ($M^+$ + 2, 4), 284 ($M^+$ + 1, 20), 283 ($M^+$, 100), 268 (14), 192 (52), 187 (20), 164 (27), 124 (15), 106 (21), 104 (13), 91 (67), 77 (30). Anal. Calcd for $C_{14}H_{13}N_5O_2$ (283.29): C, 59.36; H, 4.63; N, 24.72. Found: C, 59.26; H, 4.34; N, 24.65%.

*2-Methyl-3-(phenylazo)pyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**2d**): Yellow solid (1.08 g, 80%), m.p. 220 °C (EtOH) (Lit.[6] m.p. 222 °C).

*3-(4-Chlorophenylazo)-2-methylpyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**2e**): Orange solid (1.43 g, 94%), m.p. 240–242 °C (dioxan). IR: $\nu_{max}$ 3245, 1661, 1654 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.47 (s, 3H, $CH_3$), 5.15 (s, 2H, $CH_2$), 7.55 (d, $J$ = 8 Hz, 2H, ArH), 7.91 (d, $J$ = 8 Hz, 2H, ArH), 10.26 (s, 1H, NH). MS: *m/z* (%) 306 ($M^+$ + 2, 6), 305 ($M^+$ + 1, 34), 304 ($M^+$, 19), 303 (87), 277 (17), 207 (11), 192 (88), 164 (34), 126 (17), 124 (40), 113 (16), 111 (60), 91 (11), 76 (13). Anal. Calcd for $C_{13}H_{10}ClN_5O_2$ (303.71): C, 51.41; H, 3.32; N, 23.06. Found: C, 51.00; H, 3.52; N, 23.52%.

*3-(3-Chlorophenylazo)-2-methylpyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**2f**): Orange solid (1.23 g, 81%), m.p. 184–186 °C (EtOH). IR: $\nu_{max}$ 3389, 1690, 1653 cm$^{-1}$. NMR (DMSO-$d_6$): 2.35 (s, 3H, $CH_3$), 5.20 (s, 2H, $CH_2$), 7.06-7.81 (m, 4H, ArH), 12.42 (s, 1H, NH). MS: *m/z* (%) 303 ($M^+$, 3), 253 (44), 200 (30), 124 (100), 113 (29), 111 (87), 99 (17), 90 (19), 75 (83). Anal. Calcd for $C_{13}H_{10}ClN_5O_2$ (303.71): C, 51.41; H, 3.32; N, 23.06. Found: C, 51.63; H, 3.00; N, 23.36%.

*2-Methyl-3-(3-nitrophenylazo)pyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**2g**): Dark yellow solid (1.32 g, 84%), m.p. 256–258 °C (dioxan). IR: $\nu_{max}$ 3199, 1720, 1653 cm$^{-1}$. NMR (DMSO-$d_6$): 2.38 (s, 3H, $CH_3$), 5.15 (s, 2H, $CH_2$), 7.12–7.84 (m, 4H, ArH), 12.43 (s, 1H, NH). MS: *m/z* (%) 314 ($M^+$, 8), 313 (7), 288 (52), 246 (32), 245 (10), 166 (51), 138 (28), 124 (100), 111 (16), 92 (23), 77 (17), 76 (37). Anal. Calcd for $C_{13}H_{10}N_6O_4$ (314.26): C, 49.69; H, 3.21; N, 26.74. Found: C, 50.02; H, 3.36; N, 26.54%.

*2-Methyl-3-(4-nitrophenylazo)pyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**2h**): Dark red solid (1.26 g, 80%), m.p. 310–312 °C (AcOH) (lit.[5] m.p. 218 °C). IR: $\nu_{max}$ 3250, 1718, 1638 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.32 (s, 3H, $CH_3$), 5.14 (s, 2H, $CH_2$), 6.97 (d, $J$ = 8 Hz, 2H, ArH), 7.57 (d, $J$ = 8 Hz, 2H, ArH), 11.25 (s, 1H, NH). MS: *m/z* (%) 314 ($M^+$, 11), 246 (16), 138 (63), 124 (23),108 (100), 92 (30), 77 (12), 76 (16). Anal. Calcd for $C_{13}H_{10}N_6O_4$ (314.26): C, 49.69; H, 3.21; N, 26.74. Found: C, 49.62; H, 3.41; N, 26.91%.

*3-(4-Acetylphenylazo)-2-methylpyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**2i**): Orange solid (1.24 g, 80%), m.p. 240–242 °C (EtOH). IR: $\nu_{max}$ 3172, 1708, 1681, 1658 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.42 (s, 3H, $CH_3$), 2.94 (s, 3H, $COCH_3$), 5.18 (s, 2H, $CH_2$), 7.58 (d, $J$ = 8 Hz, 2H, ArH), 7.82 (d, $J$ = 8 Hz, 2H, ArH), 11.06 (s, 1H, NH). MS: *m/z* (%) 313 ($M^+$ + 2, 12), 312 ($M^+$ + 1, 49), 311 ($M^+$, 68), 296 (10), 200 (12), 192 (74), 164 (34), 124 (19), 119 (17), 104 (11), 91 (22), 77 (21), 69 (100). Anal. Calcd for $C_{15}H_{13}N_5O_3$ (311.30): C, 57.88; H, 4.21; N, 22.50. Found: C, 58.08, H, 4.00, N, 22.63%.

*Preparation of 3-(arylazo)-6-(arylhydrazono)-2-methylpyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-diones* (**3** *and* **4**): *general procedure*

A solution of the phenylazopyrazole **2d** (2.5 mmol) and sodium acetate trihydrate (0.33 g, 2.5 mmol) in ethanol (10 ml) was cooled to 0–5 °C and a cold solution of diazotised aniline or its derivative

(2.5 mmol) added dropwise with stirring over 30 min. The stirring was continued for 3 hrs. The solid that formed was filtered off, washed with water and crystallised from the indicated solvent to give the compounds **3a–j**. The same procedure, taking each of **2a–h** in place of **2d** and diazotised aniline, gave the respective **4a–h**.

*6-(4-Methoxyphenylhydrazono)-2-methyl-3-phenylazopyrazolo [1,5-a]pyrimidine-5,7(4H,6H)-dione* (**3a**): Dark red solid (0.48 g, 80%), m.p. 218–220 °C (dioxan/EtOH). IR: $\nu_{max}$ 3294, 3066, 1712, 1662 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.48 (s, 3H, $CH_3$), 3.78 (s, 3H, $OCH_3$), 7.03 (d, $J$ = 9 Hz, 2H, ArH), 7.41–7.64 (m, 5H, ArH), 7.91 (d, $J$ = 9 Hz, 2H, ArH), 12.20 (s, 1H, NH), 14.81 (s, 1H, NH). MS: *m/z* (%) 404 ($M^+$ + 1, 4), 403 ($M^+$, 14), 228 (28), 149 (30), 137 (46), 129 (37), 123 (37), 119 (14), 123 (37), 109 (46), 97 (100), 91 (34), 77 (20). Anal. Calcd for $C_{20}H_{17}N_7O_3$ (403.40): C, 59.55; H, 4.25; N, 24.30. Found: C, 59.50; H, 4.00; N, 24.00%.

*2-Methyl-6-(4-methylphenylhydrazono)-3-(phenylazo)pyrazolo [1,5-a]pyrimidine-5,7(4H,6H)-dione* (**3b**): Orange solid (0.50 g, 86%), m.p. 270–272 °C (AcOH). IR: $\nu_{max}$ 3426, 3060, 1721, 1659 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.30 (s, 3H, $CH_3$), 2.48 (s, 3H, $CH_3$), 7.26 (d, $J$ = 8 Hz, 2H, ArH), 7.39–7.56 (m, 5H, ArH), 7.92 (d, $J$ = 8 Hz, 2H, ArH), 12.40 (s, 1H, NH), 14.69 (s, 1H, NH). MS: *m/z* (%) 389 ($M^+$ + 2, 26), 388 ($M^+$ + 1, 100), 387 ($M^+$, 1), 298 (12), 296 (66), 229 (57), 228 (66), 212 (11), 106 (17), 105 (12), 104 (11), 91 (71), 77 (79). Anal. Calcd for $C_{20}H_{17}N_7O_2$ (387.40): C, 62.01; H, 4.42; N, 25.31. Found: C, 62.00; H, 4.40; N, 25.10%.

*2-Methyl-6-(3-methylphenylhydrazono)-3-(phenylazo)pyrazolo [1,5-a]pyrimidine-5,7(4H,6H)-dione* (**3c**): Orange solid (0.49 g, 84%), m.p. 250–252 °C (AcOH). IR (KBr) $\nu_{max}$ 3249, 3057, 1733, 1699 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.38 (s, 3H, $CH_3$), 2.48 (s, 3H, $CH_3$), 7.01–8.14 (m, 9H, ArH), 12.19 (s, 1H, NH), 13.65 (s, 1H, NH). MS: *m/z* (%) 389 ($M^+$ + 2, 1), 388 ($M^+$ + 1, 8), 387 ($M^+$, 37), 386 (39), 295 (30), 228 (26), 227 (43), 105 (17), 104 (18), 103 (15), 91 (86), 77 (100). Anal. Calcd for $C_{20}H_{17}N_7O_2$ (387.40): C, 62.01; H, 4.42; N, 25.31. Found: C, 61.98; H, 4.51; N, 25.00%.

*2-Methyl-3-(phenylazo)-6-(phenylhydrazono)pyrazolo[1,5-a] pyrimidine-5,7(4H,6H)-dione* (**3d**): Orange solid (0.47 g, 84%), m.p. 198–200 °C (AcOH) (Lit.[5] m.p. >300 °C). IR: $\nu_{max}$ 3380, 3300, 1720, 1651 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.70 (s, 3H, $CH_3$), 7.26–7.86 (m, 10H, ArH), 10.10 (s, 1H, NH), 15.00 (s, 1H, NH). MS: *m/z* (%) 375 ($M^+$ + 2, 22), 374 ($M^+$ + 1, 88), 373 ($M^+$, 1), 298 (13), 297 (78), 229 (30), 228 (39), 92 (48), 77 (100). Anal. Calcd for $C_{19}H_{15}N_7O_2$ (373.38): C, 61.12; H, 4.05; N, 26.26. Found: C, 61.00; H, 3.84; N, 26.20%.

*6-(4-Chlorophenylhydrazono)-2-methyl-3-(phenylazo) pyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**3e**): Red solid (0.54 g, 89%), m.p. 288–290 °C (AcOH). IR: $\nu_{max}$ 3325, 3074, 1720, 1662 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 1.92 (s, 3H, $CH_3$), 7.45–7.50 and 7.95–7.99 (m, 5H, ArH), 7.53 (d, $J$ = 9 Hz, 2H, ArH), 7.72 (d, $J$ = 9 Hz, 2H, ArH), 12.00 (s, 1H, NH), 14.60 (s, 1H, NH). MS: *m/z* (%) 409 ($M^+$ + 2, 29), 408 ($M^+$ + 1, 91), 407 ($M^+$, 66), 331 (21), 298 (17), 297 (97), 296 (75), 228 (77), 150 (12), 126 (14), 111 (60), 92 (74), 77 (100). Anal. Calcd for $C_{19}H_{14}ClN_7O_2$ (407.82): C, 55.96; H, 3.46; N, 24.04. Found: C, 55.83; H, 3.25; N, 24.00%.

*6-(3-Chlorophenylhydrazono)-2-methyl-3-(phenylazo) pyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**3f**): Dark orange solid (0.53 g, 86%), m.p. 256–258 °C (dioxan). IR: $\nu_{max}$ 3163, 3070, 1724, 1651 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.47 (s, 3H, $CH_3$), 7.25–7.93 (m, 9H, ArH), 12.25 (s, 1H, NH), 14.98 (s, 1H, NH). MS: *m/z* (%) 409 ($M^+$ + 2, 8), 408 ($M^+$ + 1, 26), 407 ($M^+$, 17), 167 (22), 149 (100), 139 (10), 125 (25),123 (21), 121 (17), 95 (40), 83 (56), 77 (9). Anal. Calcd for $C_{19}H_{14}ClN_7O_2$ (407.82): C, 55.96; H, 3.46; N, 24.04. Found: C, 55.85; H, 3.64; N, 23.93%.

*3-Phenylazo-2-methyl-6-(3-nitrophenylhydrazonopyrazolo[1,5-a] pyrimidine-5,7(4H,6H)-dione* (**3g**): Dark orange solid (0.52 g, 83%), m.p. 196–198 °C (dioxan). IR: $\nu_{max}$ 3300, 3058, 1701, 1658 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.48 (s, 3H, $CH_3$), 7.23–8.10 (m, 9H, ArH), 12.45 (s, 1H, NH), 15.10 (s, 1H, NH). MS: *m/z* (%) 419 ($M^+$ + 1, 16), 418 ($M^+$, 63), 341 (11), 295 (67), 228 (68), 212 (21), 192 (22), 150 (32), 122 (35), 92 (52), 91 (35), 77 (100). Anal. Calcd for $C_{19}H_{14}N_8O_4$ (418.37): C, 54.55; H, 3.37; N, 26.78. Found: C, 54.00; H, 3.24; N, 26.93%.

*2-Methyl-6-(4-nitrophenylhydrazono)-3-(phenylazo)pyrazolo[1,5-a] pyrimidine-5,7(4H,6H)-dione* (**3h**): Red solid (0.55 g, 88%), m.p. 296–298 °C (AcOH). IR: $\nu_{max}$ 3114, 3057, 1716, 1681 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.49 (s, 3H, $CH_3$), 7.42–7.54 (m, 5H, ArH), 7.86 (d, $J$ = 9 Hz, 2H, ArH), 7.93 (d, $J$ = 9 Hz, 2H, ArH), 12.45 (s, 1H, NH), 14.41 (s, 1H, NH). MS: *m/z* (%) 420 ($M^+$ + 2, 17), 419 ($M^+$ + 1, 75), 418 ($M^+$, 23), 342 (16), 296 (85), 229 (44), 228 (56), 212 (19), 150 (15), 122 (21), 92 (72), 77 (100). Anal. Calcd for $C_{19}H_{14}N_8O_4$ (418.37): C, 54.55; H, 3.37; N, 26.78. Found: C, 54.34; H, 3.21; N, 26.67%.

*6-(4-Acetylphenylhydrazono)-2-methyl-3-(phenylazo) pyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**3i**): Dark orange solid (0.54 g, 86%), m.p. 242–244 °C (dioxan/EtOH). IR: $\nu_{max}$ 3424, 3058, 1729, 1665, 1650 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.63 (s, 3H, $CH_3$), 2.70 (s, 3H, $COCH_3$), 7.27–8.05 (m, 14H, ArH), 10.10 (s, 1H, NH), 14.70 (s, 1H, NH). MS *m/z* (%) 416 ($M^+$ + 1, 56), 415 ($M^+$, 60), 361 (52), 294 (100), 268 (64), 229 (64), 224 (72), 206 (60), 158 (80), 139 (52), 111 (72), 100 (56), 91 (48). Anal. Calcd for $C_{21}H_{17}N_7O_3$ (415.41): C, 60.72; H, 4.12; N, 23.60. Found: C, 60.54, H, 4.00, N, 23.79%.

*6-(4-Ethoxycarbonylphenylhydrazono)-2-methyl-3-(phenylazo)pyrazolo[1,5-a]pyrimidine-5,7(4H,6H)-dione* (**3j**): Dark orange solid (0.57 g, 85%), m.p. 268–270 °C (DMF/EtOH). IR: $\nu_{max}$ 3325, 3062, 1739, 1712, 1658 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 1.29 (t, $J$ = 7 Hz, 3H, $CH_3$), 2.34 (s, 3H, $CH_3$), 4.25 (q, $J$ = 7 Hz, 2H, $CH_2$), 7.31-7.63 and 7.87 –7.96 (m, 5H, ArH), 7.64 (d, $J$ = 8 Hz, 2H, ArH), 7.80 (d, $J$ = 8 Hz, 2H, ArH), 12.95 (s, 1H, NH), 14.40 (s, 1H, NH). MS: *m/z* (%) 446 ($M^+$ + 1, 3), 445 ($M^+$, 4), 431 (37), 295 (42), 228 (32), 227 (29), 134 (22), 105 (13), 102 (18), 92 (60), 91 (62), 77 (91), 76 (100). Anal. Calcd for $C_{22}H_{19}N_7O_4$ (445.44): C, 59.32; H, 4.30; N, 22.01. Found: C, 59.00, H, 4.54, N, 22.00%.

*3-(4-Methoxyphenylazo)-2-methyl-6-(phenylhydrazono)pyrazolo [1,5-a]pyrimidine-5,7(4H,6H)-dione* (**4a**): Dark red solid (0.50 g, 82%), m.p. 156–158 °C (dioxan/MeOH). IR: $\nu_{max}$ 3317, 3063, 1720, 1657 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.47 (s, 3H, $CH_3$), 3.80 (s, 3H, $OCH_3$), 7.01 (d, $J$ = 9 Hz, 2H, ArH), 7.26–7.69 (m, 5H, ArH), 7.90 (d, $J$ = 9 Hz, 2H, ArH), 12.00 (s, 1H, NH), 14.63 (s, 1H, NH). MS: *m/z* (%) 405 ($M^+$ + 2, 2), 404 ($M^+$ + 1, 12), 403 ($M^+$, 44), 325 (26), 258 (16), 257 (22), 121 (34), 106 (27), 91 (35), 77 (100). Anal. Calcd for $C_{20}H_{17}N_7O_3$ (403.40): C, 59.55; H, 4.25; N, 24.30. Found: C, 59.83; H, 4.00; N, 24.15%.

*2-Methyl-3-(4-methylphenylazo)-6-(phenylhydrazono)pyrazolo[1, 5-a]pyrimidine-5,7(4H,6H)-dione* (**4b**): Orange solid (0.46 g, 80%), m.p. 280–281 °C (dioxan/MeOH). IR: $\nu_{max}$ 3234, 3061, 1725, 1663 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.36 (s, 3H, $CH_3$), 2.49 (s, 3H, $CH_3$), 7.28–7.53 (m, 5H, ArH), 7.66 (d, $J$ = 9 Hz, 2H, ArH), 7.84 (d, $J$ = 9 Hz, 2H, ArH), 12.20 (s, 1H, NH), 14.64 (s, 1H, NH); MS *m/z* (%) 389 ($M^+$ + 2, 1), 388 ($M^+$ + 1, 9), 387 ($M^+$, 35), 386 (46), 310 (24), 242 (19), 241 (22), 105 (32), 90 (56), 77 (100). Anal. Calcd for $C_{20}H_{17}N_7O_2$ (387.40): C, 62.01; H, 4.42; N, 25.31. Found: C, 62.00; H, 4.25; N, 25.14%.

*3-(4-Chlorophenylazo)-2-methyl-6-(phenylhydrazono)pyrazolo [1,5-a]pyrimidine-5,7(4H,6H)-dione* (**4e**): Dark yellow solid (0.53 g, 86%), m.p. 144–146 °C (dioxan/EtOH). IR: $\nu_{max}$ 3380, 3063, 1720, 1658 cm$^{-1}$. NMR (DMSO-$d_6$): $\delta_H$ 2.49 (s, 3H, $CH_3$), 7.28–7.53 (m, 5H, ArH), 7.56 (d, $J$ = 8 Hz, 2H, ArH), 7.98 (d, $J$ = 8 Hz, 2H, ArH), 12.32 (s, 1H, NH), 14.64 (s, 1H, NH). MS: *m/z* (%) 409 ($M^+$ + 2, 11), 408 ($M^+$ + 1, 14), 407 ($M^+$, 28), 407 (28), 406 (32), 330 (24), 261 (18), 125 (24), 113 (11), 111 (31), 91 (22), 77 (100). Anal. Calcd for $C_{19}H_{14}ClN_7O_2$ (407.82): C, 55.96; H, 3.46; N, 24.04. Found: C, 55.82; H, 3.43; N, 24.35%.

*3-(3-Chlorophenylazo)-2-methyl-6-(phenylhydrazono)pyrazolo[1,5-a] pyrimidine-5,7(4H,6H)-dione* (**4f**): Dark orange solid (0.51 g, 83%), m.p. 238–239 °C (dioxan). IR: $\nu_{max}$ 3244, 3065, 1705, 1669 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.51 (s, 3H, $CH_3$), 7.34-8.03 (m, 9H, ArH), 12.17 (s, 1H, NH), 13.80 (s, 1H, NH). MS: *m/z* (%) 409 ($M^+$ + 1, 14), 408 ($M^+$, 15), 407 (37), 332 (48), 330 (54), 262 (50), 200 (34), 192 (50), 127 (46), 125 (32),124 (53), 90 (28), 77 (53). Anal. Calcd for $C_{19}H_{14}ClN_7O_2$ (407.82): C, 55.96; H, 3.46; N, 24.04. Found: C, 55.84; H, 3.43; N, 24.40%.

*2-Methyl-3-(3-nitrophenylazo)-6-(phenylhydrazono)pyrazolo[1,5-a] pyrimidine-5,7(4H,6H)-dione* (**4g**): Dark orange solid (0.51 g, 82%), m.p. 272–274 °C (dioxan). IR: $\nu_{max}$ 3216, 3086, 1720, 1656 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.42 (s, 3H, $CH_3$), 7.25–7.62 (m, 9H, ArH), 12.19 (s, 1H, NH), 14.25 (s, 1H, NH). MS: *m/z* (%) 418 ($M^+$, 12), 246 (34), 192 (13), 166 (22), 153 (21), 150 (100), 125 (21), 124 (69), 122 (38), 92 (42), 77 (42). Anal. Calcd for $C_{19}H_{14}N_8O_4$ (418.37): C, 54.55; H, 3.37; N, 26.78. Found: C, 54.81; H, 3.00; N, 26.74%.

*2-Methyl-3-(4-Nitrophenylazo)-6-(phenylhydrazono)pyrazolo[1,5-a] pyrimidine-5,7(4H,6H)-dione* (**4h**): Dark red solid (0.51 g, 81%), m.p. 292–294 °C (dioxan). IR: $\nu_{max}$ 3219, 3100, 1710, 1655 cm$^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.35 (s, 3H, $CH_3$), 7.14–7.54 (m, 5H, ArH), 7.58 (d, $J$ = 8 Hz, 2H, ArH), 7.81 (d, $J$ = 8 Hz, 2H, ArH), 12.33 (s, 1H, NH), 15.32 (s, 1H, NH). MS: *m/z* (%) 419 ($M^+$ + 1, 6), 418 ($M^+$, 11), 272 (74), 246 (21), 242 (12), 150 (100), 138 (23), 124 (18), 122 (28), 108 (25), 93 (31), 77 (33). Anal. Calcd for $C_{19}H_{14}N_8O_4$ (418.37): C, 54.55; H, 3.37; N, 26.78. Found: C, 54.35; H, 3.02; N, 26.59%.

*3-(4-Acetylphenylazo)-2-methyl-6-(phenylhydrazono)pyrazolo [1,5-a]pyrimidine-5,7(4H,6H)-dione* (**4i**): Dark red solid (0.50 g,

80%), m.p. 250–252 °C (dioxan/MeOH). IR: $\nu_{max}$ 3385, 3061, 1720, 1670, 1656 $cm^{-1}$. NMR ($CDCl_3$): $\delta_H$ 2.27 (s, 3H, $CH_3$), 2.43 (s, 3H, $COCH_3$), 7.15–7.61 (m, 5H, ArH), 7.63 (d, $J$ = 8 Hz, 2H, ArH), 7.81 (d, $J$ = 8 Hz, 2H, ArH), 12.45 (s, 1H, NH), 14.64 (s, 1H, NH). MS: *m/z* (%) 416 ($M^+$ + 1, 8), 415 ($M^+$, 21), 414 (25), 390 (21), 270 (15), 221 (29), 119 (27), 106 (20), 105 (16), 91 (63), 77 (100). Anal. Calcd for $C_{21}H_{17}N_7O_3$ (415.41): C, 60.72; H, 4.12; N, 23.60. Found: C, 60.35, H, 4.36, N, 23.45%.

*$pK_a$ Determination of compounds* **3** *and* **4**

The acid dissociation constants of the compounds **3** and **4** were determined potentiometrically in 50% dioxan–water mixture at 25±0.1 °C and ionic strength ($KNO_3$) of 0.1 M. A Metrohm 686 titroprocessor equipped with 665 Dosimat was employed. The electrode and the titroprocessor were calibrated with standard Beckman buffer solutions of pH 4.01 and 7.00. The pH meter reading B recorded in 50% dioxan–water solution was converted to hydrogen ion concentration [$H^+$] by means of the widely used relation of van Uitert and Hass,[21] namely:

$$\log [H^+] = B + \log U_H$$

where $\log U_H$ is the correction factor for the solvent composition and ionic strength used for which B is read. The value of $\log U_H$ for the medium in our work was found to be 0.21. A carbonate-free sodium hydroxide titrant was prepared and standardised against potassium hydrogen phthalate solution.

The experimental procedure followed in the determination of $pK_a$ values and their calculations, by the method of least squares, from the titrant volume-pH data using the relation:

$$pK_a = pH_i - \log V_i/(V_e - V_i)$$

where $pH_i$ is the corrected pH value of the solution when the volume of the added titrant is $V_i$ and $V_e$ is the volume of the titrant at the equivalent point as previously described.[22] The calculations of the $pK_a$ values were carried out using the computer program MINIQUAD-75.[23] The $pK_a$ values obtained were reproducible to within ± 0.02 $pK_a$ unit. The results are recorded in Tables 1 and 2.

*Received 21 March 2008; accepted 5 June 2008*
*Paper 08/5172 doi:10.3184/030823408X339782*
*Published online: 26 August 2008*

## References

1 A.S. Shawali and M.A.N. Mosselhi, *J. Heterocyclic Chem.,* 2003, **40**, 725.
2 A.S. Shawali, M.A. Abdallah and M.E.M. Zayed, *J. Chinese Chem. Soc.*, 2002, **49**, 1035.
3 A.S. Shawali, M.H. Abdel Kader and F.M.A. Altalbawy, *Tetrahedron*, 2002, **58**, 2875.
4 A.S. Shawali, M.A. Abdallah, M.A.N. Mosselhi and Y.F. Mohamed, *Z. Naturforsch.*, 2002, **57b,** 552.
5 D.W. Rangnekar and S.S. Puro, *Indian J. Fibre Textile Res.,* 1990, **15**, 23.
6 M.H. Elnagdi, M.M.M. Sallam, H.M. Fahmy, S.A. Ibrahim and M.A.M. Elias, *Helv. Chim. Acta*, 1976, **59**, 551.
7 M.N. Mosselhi, M.A. Abdallah, Y.F. Mohamed and A.S. Shawali, *Phosphorus, Sulfur Silicon,* 2002, **177**, 487.
8 A.S. Shawali, I.F. Zeid, M.H. Abdelkader and F.M.A. Altalbawy, *J. Chinese Chem. Soc.*, 2001, **48,** 65.
9 M.N. Mosselhi, M.A. Abdallah, S.M. Riyadh, A.E. Harhash and A.S. Shawali, *J. Prakt. Chem.*, 1998, **340**, 160.
10 A.S. Shawali, N.M.S. Harb and K.O. Badahdah, *J. Heterocycl. Chem.,* 1985, **22**, 1397.
11 C.D. Johnson, *The Hammett Equation*, Cambridge University Press, 1973.
12 A.S. Shawali, M.A.N. Mosselhi and T.A. Farghaly, *J. Chem. Res.*, 2007, 479.
13 A.S. Shawali, M.S. Rizk, A.O. Abdelhamid, M.A. Abdallah, C. Parkanyi and M.E. Wojciechowska, *Heterocycles*, 1983, **20**, 2211.
14 A.S. Shawali, H.M. Hassaneen and M.A. Hanna, *Heterocycles,* 1981, **15,** 697.
15 A.E. Elhilaly, A.S. Shawali and M.A. Madkour, *Inorg. Chim. Acta,* 1979, **36,** 179.
16 K.U. Sadek, N.S. Ibrahim and M.H. Elnagdi, *Arch. Pharm. (Weinheim)*, 1988, **321**, 141.
17 A.S. Shawali, E.S.S. Darwish and M.A. Farag, *Asian J. Spect.,* 2007, **11**, 115.
18 V.B. Hirsch, *Liebigs Ann. Chem*., 1965, **690**, 33.
19 M.H. Elnagdi, N.H. Taha, F.A. Abd El All, R.M. Abdel Motaleb and F.F. Mahmoud, *Collect. Czech. Chem. Commun.,* 1989, **54**, 1082.
20 F. Karci and A. Demircali, *Dyes Pigments*, 2007, **74**, 288.
21 L.G. Van Uitert and C.G. Haas, *J. Am. Chem. Soc*., 1953, **75**, 451.
22 A. Albert and E.P. Serjeant, *The Determination of Ionisation Constants,* Chapman and Hall, London, 1971.
22 P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.