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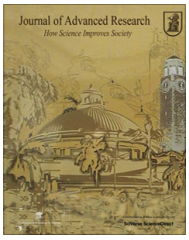

ORIGINAL ARTICLE

A new one-pot synthesis of novel hetarylazo-heterocyclic colorants and study of their solvatochromic properties

Ahmad S. Shawali *, **Magda A. Abdallah**, **Mohamed A. Kandil**

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

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ABSTRACT

A simple synthetic strategy for synthesis of new series of hetarylazo-heterocycles is described. The effects of solvent on their electronic absorption spectra were analyzed using Kamlet–Taft equation. The results of fitting coefficients indicated that the solvatochromism of the studied compounds is mainly due to the solvent polarity rather than the solvent basicity and acidity.

Introduction

A literature survey reveals that most of the reported hetarylazo heterocycles were usually prepared by coupling of diazotized heterocyclic amines with the appropriate heterocyclic nucleophilic reagents [1] or by reactions of hydrazonoyl halides with the appropriate reagents [2]. In continuation of our studies on exploring the utility of hydrazonoyl halides in synthesis of arylazo derivatives of heterocyclic compounds [3–10], it was thought interesting to study the synthesis of new 3-chloro-1,5-*bis*(hetaryl)formazans and explore their utility in synthesis of novel hetarylazo derivatives of various heterocycles. This is because, although 3-chloro-1,5-di-arylformazans, Ar—N═N—C(Cl)═NNHAr, have been known since 1946 [11–13], little attention, if there is any, has been given hitherto to the related 3-chloro-1,5-*bis*(hetaryl)formazans of the general formula, Het—N═N—C(Cl)═NNH—Het. The adopted synthetic strategy for the target azo colorants in this study depends on 1,5-electrocyclization of the nitrilimines derived from the target new 3-chloro-1,5-bis(hetaryl)-formazans (Scheme 1). In addition, as many arylazo derivatives of heterocyclic compounds have found various applications in industry

* Corresponding author.
E-mail address: as_shawali@mail.com (A.S. Shawali).
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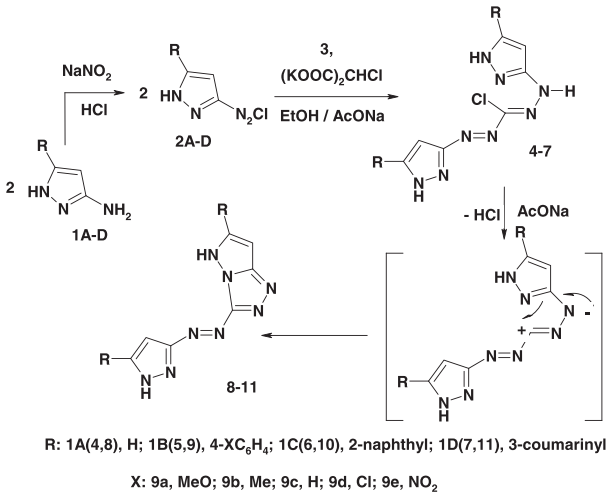


Scheme 1

including hair dyeing, disperse dyes, ink-jet inks, photodynamic therapy, nonlinear optical systems and laser materials [14,15], it was thought interesting to study the solvatochromic properties of the new colorants prepared via application of Kamlet–Taft equation [16,17]. The knowledge of the results of such correlations is useful prior exploring the applications of the target azo colorants.

Experimental

All melting points were determined on a Gallenkamp apparatus. Solvents were generally distilled and dried by standard literature procedures prior to use. The IR spectra were measured on a Pye-Unicam SP300 instrument in potassium bromide discs. The ^{1}H NMR spectra were recorded on a Varian Mercury VXR-300 MHz spectrometer and the chemical shifts δ down field from tetramethylsilane (TMS) as an internal standard. The mass spectra were recorded on a GCMS-Q1000-EX Shimadzu and GCMS 5988-A HP spectrometers, the ionizing voltage was 70 eV. Electronic absorption spectra were recorded on Perkin–Elmer Lambada 40 spectrophotometer. Elemental analyses were carried out by the Microanalytical Center of Cairo University, Giza, Egypt. Both diethyl chloromalonate and potassium chloromalonate were prepared as previously described [18]. 5-Amino-1*H*-pyrazole **1A**, 3-amino [1,2,4]triazole **1E** and 2-aminobenzimidazole **1F** were purchased from Sigma Aldrich. 5-Amino-3-aryl-1*H*-pyrazoles **1B**, 5-amino-3-(2-naphthyl)-1*H*-pyrazole **1C** and 5-amino-3-(coumarin-3-yl)-1*H*-pyrazole **1D** were prepared by literature procedures [19,20].

*Synthesis of 3-hetarylazo heterocycles (**8**–**13**)*

General procedure – to a cold solution of the appropriate heterocyclic amine **1** (0.01 mol) solution in hydrochloric acid (3 mL, 1 M) was added a solution of sodium nitrite (0.7 g, 0.01 mol) dropwise while stirring the reaction mixture and being cooled in an ice bath. The resulting diazotized amine solution was then added portionwise to a stirred cold (0–5 °C) solution of a mixture of potassium chloromalonate (1.07 g, 0.005 mol) and sodium acetate (1 g, 0.01 mol) in water (20 mL). After the addition was completed, the reaction mixture was stirred for further 1 h while being cooled in an ice bath, then left overnight in a refrigerator. The solid product, that precipitated, was filtered off, dried and then crystallized from the appropriate solvent to give the corresponding hetarylazo derivative. The compounds **8–13** prepared and their physical constants are listed below.

3-[(1H-pyrazol-5-yl)azo]pyrazolo[5,1-c][1,2,4]triazole (**8**): yellowish orange solid, (0.76 g, 75%), mp. 190–195 °C (dioxane), IR: υ (KBr) 3122, 3312 (NH) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.85–8.15 (m, 4H, Het-H), 9.00 (s, 1H, NH), 9.65 (s, 1H, NH). MS, *m*/*z* (%): 202 (M$^+$, 64), 190 (13), 148 (19), 135 (40), 122 (100), 107 (88), 95 (50), 77 (45), 65 (50). Anal Calcd for $C_7H_6N_8$ (202.18): C, 41.58; H, 2.99; N, 55.42. Found: C, 41.60; H, 2.69; N, 55.20%.

3-[3-(4-Methoxyphenyl)-1H-pyrazol-5-yl)azo]-6-(4-methoxyphenyl)-1H-pyrazolo[5,1-c]-[1,2,4]triazole (**9a**): yellow solid, (1.6 g, 78%), mp. 140–142 °C (ethanol), IR: υ (KBr) 3081, 3190 (NH) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 3.76 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.97–7.50 (m, 8H, ArH), 7.70–7.95 (m, 2H, Het-H), 8.80 (s, 1H, NH), 9.20 (s, 1H, NH). MS, *m*/*z* (%):414 (M$^+$, 75), 375 (60), 350 (58), 310 (53), 286 (64), 251 (68), 195 (58), 190 (100), 158 (55), 117 (67), 109 (28), 77 (60). Anal Calcd for $C_{21}H_{18}N_8O_2$ (414.43): C, 60.86; H, 4.38; N, 27.04. Found: C, 60.90; H, 4.29; N, 27.20%.

3-[3-(4-Methylphenyl)-1H-pyrazol-5-yl)azo]-6-(4-methylphenyl)-1H-pyrazolo[5,1-c][1,2,4] triazole (**9b**): yellow solid, (1.5 g, 77%), mp. 152–154 °C (EtOH), IR: υ (KBr) 3181, 3300 (NH) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 2.29 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 7.48–7.59 (m, 8H, ArH), 7.70–7.95 (m, 2H, Het-H), 8.95 (s, 1H, NH), 9.10 (s, 1H, NH). MS, *m*/*z* (%): 382 (M$^+$, 26), 368 (80), 353 (50), 310 (53), 286 (64), 248 (100), 220 (82), 190 (90), 186 (25), 160 (42), 117 (14), 109 (55), 77 (91). Anal Calcd for $C_{21}H_{18}N_8$ (382.43): C, 65.95; H, 4.74; N, 29.30. Found: C, 65.82; H,4.70; N, 29.52%.

3-[(3-Phenyl-1H-pyrazol-5-yl)azo]-6-phenyl-1H-pyrazolo [5,1-c][1,2,4]triazole (**9c**): yellow solid, (1.5 g, 85%), mp. 150–153 °C (dioxane), IR: υ (KBr) 3151, 3209 (NH) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.42–7.52 (m, 10H, ArH), 8.13–8.33 (m, 2H, Het-H), 8.91 (s, 1H, NH), 9.20 (s, 1H, NH). MS, *m*/*z* (%): 354 (M$^+$, 5.5), 328 (10), 311 (15), 285 (18), 250 (25), 196 (18), 158 (100), 129 (30), 102 (40), 77 (65). Anal Calcd for $C_{19}H_{14}N_8$ (354.30): C, 64.40; H, 3.98; N, 31.62. Found: C, 64.20; H, 3.90; N, 31.82%.

3-[3-(4-Chlorophenyl)-1H-pyrazol-5-yl)azo]-6-(4-chlorophenyl)-1H-pyrazolo[5,1-c]-[1,2,4] triazole (**9d**): golden yellow solid, (1.73 g, 82%), mp. 165–167 °C (dioxane), IR: υ (KBr) 3040, 3236 (NH) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.43–7.75 (m, 8H, ArH), 8.24–8.51 (m, 2H, Het-H), 9.54 (s, 1H, NH), 10.07 (s, 1H, NH). MS, *m*/*z* (%): 423 (M$^+$, 25), 415 (30), 320 (70), 300 (26), 281 (40), 244 (61), 231 (63), 193 (36),181 (29), 155 (33), 139 (90), 111 (60), 80 (100). Anal Calcd for $C_{19}H_{12}Cl_2N_8$ (423.27): C, 53.92; H, 2.86; N, 26.47. Found: C, 54.14; H, 3.01; N, 26.19%.

3-[3-(4-Nitrophenyl)-1H-pyrazol-5-yl)azo]-6-(4-nitrophenyl)-1H-pyrazolo[5,1-c][1,2,4]- triazole (**9e**): yellow solid, (1.95 g, 88%), mp. 155–157 °C (EtOH), IR: υ (KBr) 3240, 3306 (NH) cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.48–7.59 (m, 8H, ArH), 7.78–7.91 (m, 2H, Het-H), 8.97 (s, 1H, NH), 9.28 (s, 1H, NH). MS, *m*/*z* (%): 444 (M$^+$, 80), 431 (65), 416 (50), 391 (85), 370 (77), 359 (60), 316 (70), 303 (63), 281 (100), 244

(61), 231 (63), 190 (90), 184 (58), 159 (61), 112 (94), 108 (65), 76 (93). Anal Calcd for $C_{19}H_{12}N_{10}O_4$ (444.37): C, 51.36; H, 2.72; N, 31.52. Found: C, 51.90; H, 2.52; N, 31.29%.

3-[3-(2-Naphthyl-1H-pyrazol-5-y)lazo]-6-(2-naphthyl)-1H-pyrazolo[5,1-c]-[1,2,4]triazole (**10**): yellow solid, (1.68 g, 74%), mp. 225–228 °C (dioxane), IR: υ (KBr) 3055,3247 (NH) cm^{-1}. ^1H NMR (DMSO-d_6) δ 7.64–7.85 (m, 14H, ArH), 8.35–8.59 (m, 2H, Het-H), 9.83 (s, 1H, NH), 10.54 (s, 1H, NH). MS, *m/z* (%):454 (M^+, 10), 318 (40), 305 (21), 246 (18), 235 (14), 209 (83), 181 (36), 153 (70), 127(100), 105 (27), 85 (25), 67 (38). Anal Calcd for $C_{27}H_{18}N_8$ (454.50): C, 71.35; H, 3.99; N, 24.66. Found: C, 71.60; H, 3.85; N, 24.82%.

3-[3-(Coumarin-3-yl)pyrazol-5-yl)azo]-6-(coumarin-3-yl)-1H-pyrazolo[5,1-c]-[1,2,4]-triazole (**11**): reddish yellow solid, (1.9 g, 78%), mp. 270–272 °C (dioxane), IR: υ (KBr) 3147, 3317 (NH), 1666 (CO) cm^{-1}. ^1H NMR (DMSO-d_6) δ 7.54–7.73 (m, 10H, ArH), 8.21–8.459 (m, 2H, Het-H), 9.88 (s, 1H, NH), 10.59 (s, 1H, NH). MS, *m/z* (%): 490 (M^+, 50), 450 (40), 414 (32), 398 (31), 302 (31), 245 (28), 230 (22), 158 (30), 127 (100), 100 (70), 85 (40), 77 (22). Anal Calcd for $C_{25}H_{14}N_8O_4$ (490.44): C, 61.23; H, 2.88; N, 22.85. Found: C, 61.00; H, 2.95; N, 22.69%.

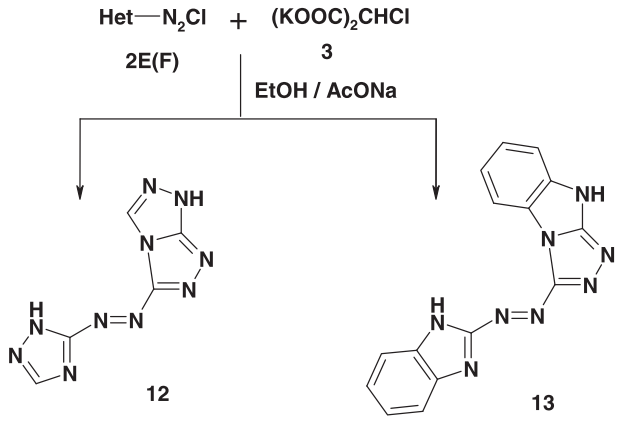
3-[(1,2,4-Triazol-3-yl)azo][1,2,4]-triazolo[3,4-c][1,2,4]triazole (**12**): reddish orange solid, (0.82 g, 80%), mp. > 300 °C (DMF), IR: υ (KBr) 3128, 3367 (NH) cm^{-1}. ^1H NMR (DMSO-d_6) δ 8.87–8.60 (m, 2H, Het-H), 13.32 (s, 1H, NH), 14.55 (s, 1H, NH). MS, *m/z* (%): 204 (M^+, 40), 186 (70), 138 (70), 137 (70), 133 (100), 119 (30), 92 (80), 65 (50). Anal Calcd for $C_5H_4N_{10}$ (204.15): C, 29.42; H, 1.97; N, 68.61. Found: C, 29.20; H, 1.90; N, 68.49%.

3-[(Benzimidazol-2-yl)azo]benzimidazo[2,1-c][1,2,4]triazole (**13**): yellow solid, (1.3 g, 87%), mp. 188–190 °C (dioxane), IR: υ (KBr) 3082, 3282 (NH) cm^{-1}. ^1H NMR (DMSO-d_6) δ 6.83–6.95 (m, 8H, ArH), 10.55 (s, 1H, NH), 11.25 (s, 1H, NH). MS, *m/z* (%): 302 (M^+, 30), 277 (80), 250 (89), 206 (70), 186 (65), 145 (25), 138 (70), 186 (40), 137 (88), 133 (90), 119 (50), 92 (89), 65 (100). Anal Calcd for $C_{15}H_{10}N_8$ (302.30): C, 59.60; H, 3.33; N, 37.07. Found: C, 59.42; H, 3.15; N, 37.13%.

Results and discussion

Synthesis and characterization

The required potassium chloromalonate was prepared as previously described [18]. Treatment of potassium chloromalonate with two molar equivalents of each of the appropriate diazotized 3-aminopyrazoles **2A–D** in dioxane–water solution in the presence of sodium acetate, gave a single product in each case as evidenced by TLC analysis of the crude product. The structures of the isolated compounds were elucidated on the basis of their microanalyses and spectral data (MS, IR and ^1H NMR) (see Experimental). For example, the IR spectra of the compounds prepared showed, in each case, two NH bands in the regions υ 3140–3240 and 3212–3367 cm^{-1}. Their ^1H NMR spectra, in addition to the aromatic proton signals, they revealed two common characteristic singlet signals in the regions δ 8.80–13.32 and 9.10–14.55 due to the resonances of the NH protons. Furthermore, the electronic absorption spectrum of each of the studied compounds exhibits, in a given solvent, two absorption bands in the regions λ 280–350 and 400–450 nm. The results are summarized in Table 1. As shown, each compound exhibits an intense absorption band in the region 400–450 nm similar to that of typical azo-chromophores [10,21,22]. These spectral data together with the results of elemental analyses indicate that the products isolated from the studied reactions are the corresponding hetarylazo compounds **8–11** (Scheme 1). Such structural assignment is further confirmed by their mass spectra (see Experimental).



Het: 2E, 1,2,4-triazol-5-yl; 2F, Benzimidazol-2-yl

Scheme 2

Similar treatment of potassium chloromalonate with two molar equivalents of each of the diazotized 5-amino-1,2,4-triazole **2E** and 2-aminobenzimidazole **2F** under the same

Table 1 Electronic absorption spectral data of compounds **9a–e** and **10–11** in various solvents.

Compd. no.	Solvent/λ_{max} (log ε)				
	Ethanol	1,4-Dioxane	Chloroform	Methanol	Acetonitrile
9a	419(4.57); 318 (4.87)	420 (4.48); 316 (4.79)	417 (4.39); 314 (4.83)	418 (4.54); 319 (4.95)	416 (4.56); 315 (4.88)
9b	419(4.59); 320 (4.92)	420 (4.68); 319 (4.98)	415 (4.55); 318 (4.85)	416(4.60); 321 (4.86)	414 (4.63); 315 (4.92)
9c	418(4.42); 314(4.88)	419 (4.52); 316 (4.92)	412 (4.46); 314 (4.85)	413 (4.51); 318 (4.92)	410 (4.56); 317 (4.89)
9d	419(4.78); 315 (4.98)	421 (4.85); 310 (5.01)	417 (4.77); 309 (4.94)	416 (4.89); 307 (5.02)	418 (4.74); 315 (4.97)
9e	423(4.78); 319 (4.99)	423 (4.81); 315 (5.00)	417 (4.75); 314 (4.95)	415 (4.84); 318 (4.97)	420 (4.80); 316 (4.92)
10	425(4.85); 315 (4.92)	428 (4.90); 319 (4.98)	420 (4.82); 318 (4.94)	419 (4.86); 312 (4.96)	421 (4.83); 317 (4.93)
11	428(4.80); 312 (4.90)	432 (4.85); 300 (4.95)	425 (4.84); 288 (4.93)	423 (3.87); 300 (4.96)	426 (4.83); 300 (4.92)

Table 2 Solvent parameters [13].

Solvent	π^*	β	α
Ethanol	0.54	0.77	0.83
Dioxane	0.55	0.37	0.0
Chloroform	0.58	0.0	0.44
Methanol	0.60	0.62	0.93
Acetonitrile	0.75	0.31	0.19

conditions yielded the corresponding azo derivatives **12** and **13**, respectively (Scheme 2). The structures of the latter compounds were elucidated on the basis of their microanalyses and spectral data (MS, IR and ^{1}H NMR) (see Experimental).

To account for the formation of the products **8–13**, it is suggested, as depicted in Scheme 1 that the reactions start with the formation of the corresponding 3-chloro-1,5-dihetarylformazans as intermediates. Under the employed reaction conditions, the latter undergo *in situ* dehydrochlorination to form the corresponding nitrilimines, which in turn undergo 1,5-electrocyclization to give the corresponding azo compounds **8–13** as end products. This suggested pathway is consistent with literature reports on 1,5-electrocyclization of N-hetaryl-nitrilimines [19] and synthesis of chloroformazans [23].

Solvatochromic properties

Before exploring the utility of the compounds prepared as colorant reagents, it was thought necessary to shed some light on their solvatochromic properties. For this purpose, the electronic absorption spectra of each of the compounds **8–11** were recorded in a series of five solvents of different solvation character namely ethanol, 1,4-dioxane, chloroform, methanol and acetonitrile at a concentration of 1×10^{-6} mol/L over the range λ 200–800 nm. The results are summarized in Table 1. The effects of solvent polarity and hydrogen bonding on the electronic absorption spectra of the studied compounds **9a–e**, **10** and **11** were interpreted by means of the linear solvation energy relationship (LSER) namely Kamlet–Taft equation (Eq. (1)) [16,17],

$$\tilde{\upsilon} = \upsilon^o + s\pi^* + b\beta + a\alpha \quad (1)$$

where π^* is the measure of solvent dipolarity/polarizabilty, β is the scale of the solvent hydrogen bond acceptor basicity, α is the scale of the solvent hydrogen-bond donor acidity and υ^o is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients s, b and a in Eq. (1) measure the relative susceptibilities of the solvent-dependent solute property (absorption frequencies) to the indicated solvent parameters. The values of the solvent parameters are given in Table 2.

The correlation of the spectroscopic data were carried out by multiple linear regression analysis using Eq. (1). The results are given in Table 3. As shown, the values (0.890–0.990) of the correlation coefficient (r) indicate that the absorption frequencies for the studied azo compounds in the selected solvents show satisfactory correlation with the solvent parameters π^*, β and α. The degree of success of Eq. (1) is shown also in Fig. 1 by means of a plot of calculated υ_{max} versus observed υ_{max} in 1,4-dioxane (Table 4). The equation of the regression line is:

$$\upsilon_{exp} = 2.493 + 0.966\upsilon_{calcd} \quad (2)$$

with correlation coefficient $r = 0.970$ and standard error $s \pm 0.220$.

Furthermore, as the coefficients of the solvent parameters measure the relative susceptibilities of the solvent-dependent solute property namely the absorption frequencies to the indicated solvent parameters, it is clear that the negative sign of the α-coefficient indicates a bathochromic shift and the positive sign of the β-coefficient indicates a hypsochromic shift. The percentage contributions of solvatochromic parameters for the studied azo dyes **9–11** are depicted in Table 5. As shown

Table 3 Regression fits to solvatochromic parameters (Eq. (1)).[a,b]

Compd. no.	Equation	r; $\pm s$
9a	$\upsilon_{max} = (70.05 + 1.98\pi^* - 0.138\beta + 0.463\alpha)10^{13}$	$r = 0.920$; $s = \pm 0.195$
9b	$\upsilon_{max} = (69.53 + 4.15\pi^* - 1.072\beta + 0.795\alpha)10^{13}$	$r = 0.990$; $s = \pm 0.020$
9c	$\upsilon_{max} = (69.32 + 5.54\pi^* - 1.32\beta + 0.723\alpha)10^{13}$	$r = 0.970$; $s = \pm 0.205$
9d	$\upsilon_{max} = (70.10 + 1.78\pi^* - 0.76\beta + 0.97\alpha)10^{13}$	$r = 0.974$; $s = \pm 0.153$
9e	$\upsilon_{max} = (70.15 + 2.13\pi^* - 1.62\beta + 1.53\alpha)10^{13}$	$r = 0.850$; $s = \pm 0.640$
10	$\upsilon_{max} = (68.20 + 4.362\pi^* - 1.578\beta + 1.702\alpha)10^{13}$	$r = 0.978$; $s = \pm 0.240$
11	$\upsilon_{max} = (67.87 + 3.51\pi^* - 1.160\beta + 1.624\alpha)10^{13}$	$r = 0.981$; $s = \pm 0.217$

[a] r, Correlation coefficient.
[b] $\pm s$, Standard error of the estimate.

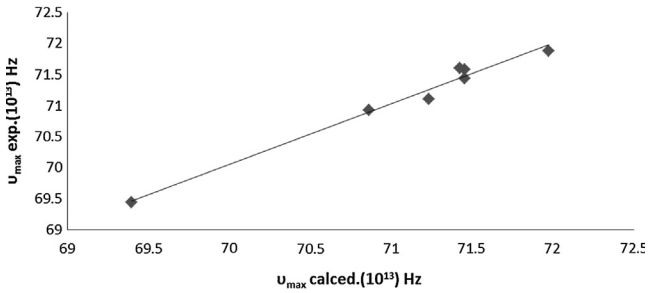


Fig. 1 The plot of observed υ_{max} against calculated υ_{max} by Eq. (1) for compounds **9**–**11** in different solvents.

Table 4 Experimental and calculated values of υ_{max} of compounds **9**–**11** in 1,4-dioxane.

Cmpound no.	υ_{max} Calcd. (10^{13}) Hz	υ_{max} Exp. (10^{13}) Hz
9a	71.642	71.455
9b	71.429	71.454
9c	71.872	71.973
9d	70.750	70.863
9e	70.820	71.236
10	70.094	71.427
11	69.444	69.396

Table 5 Percentage contribution of solventochromic parameters.[a]

Compd. no.	$P\pi^*$ (%)	$P\beta$ (%)	$P\alpha$ (%)
9a	76.70	5.00	17.00
9b	68.97	17.82	13.21
9c	73.01	17.41	9.53
9d	50.08	21.60	27.62
9e	40.37	30.68	28.94
10	57.10	20.64	22.27
11	55.77	18.43	25.80

[a] $Pi\ (\%) = i\ (100)/[s + b + a]$.

for all of the compounds studied, the solvatochromism is due to the solvent polarity rather than the solvent basicity and acidity.

Conclusions

In summary, we have developed a new one-pot method that offers a convenient and efficient procedure for synthesis of various hetarylazo heterocycles. Expanding the scope of this method will be useful to the synthesis of other interesting hetarylazo heterocyclic compounds. In addition, the results of the study of the effects of solvent on the electronic absorption spectra of the studied compounds using Kamlet–Taft equation indicated that their color is mainly influenced by the solvent polarity rather than the solvent basicity and acidity.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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