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Synthesis and tautomeric structure of 3,7-bis(arylazo)-6-methyl-2-phenyl-1*H*-imidazo[1,2-*b*]pyrazoles in ground and excited states

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ABSTRACT

Three series of 3,7-bis(arylazo)-6-methyl-2-phenyl-1*H*-imidazo-[1,2-*b*]pyrazoles were prepared starting from *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides and 5-amino-4-arylazo-3-methyl pyrazoles. The acid dissociation constants p*K* and p*K** in both the ground and excited states, respectively, were determined and correlated with the Hammett equation. The results of such correlations together with the spectroscopic data indicated that the title compounds exist predominantly in the 1*H*-bis(arylazo) form in both ground and excited states.

1. Introduction

Arylazo heterocycles are a versatile class of colored organic compounds that have attracted the interest of many research groups including us as they have many industrial applications in the fields of textiles, papers, leather, additives, foodstuffs, cosmetics, laser materials, xerography, and laser printing.[1–7] In addition, other azo dyes have found uses as organic second order non-linear optical (NLO) materials suitable for applications such as harmonic generation and optical switching.[8] Others are used in photodynamic therapy.[9] Furthermore, many derivatives of the azapentalene ring system were reported to have diverse utilities in the fields of material science and theoretical chemistry[10] and some of them were reported to have biological and pharmacological activities.[11–14] In view of these facts and in continuation of our studies on the use of hydrazonoyl halides as useful precursors for the synthesis of various arylazo heterocycles,[15] it was considered worthwhile to synthesize the title compounds and determine their tautomeric structure prior to exploring their applications. This is because the target bis-arylazo compounds can have one or more of four tautomeric structures (Fig. 1).

2. Results and discussion

The starting 3-iminobutyronitrile **1**,[16] 2-arylhydrazono-3-iminobutyronitrile **2**,[17] and hydrazonoyl bromides **4**[18] were prepared by literature methods. Treatment of **2** with hydrazine hydrate in refluxing ethanol afforded the respective 5-amino-4-arylzo-3-methylpyrazoles **3** in good yields (Scheme 1). The structures of the latter derivatives **3a–g** were confirmed by their IR, NMR, mass

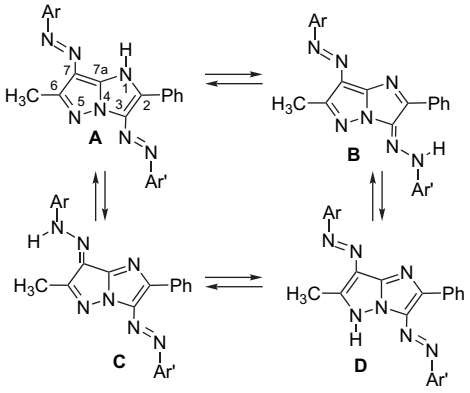

Figure 1.

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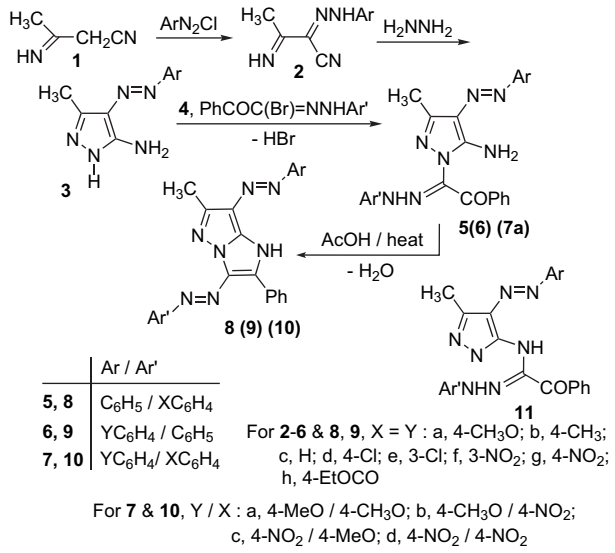

Scheme 1.

spectra, elemental analysis and comparison with authentic samples.

Reaction of **3c** with each of the hydrazonoyl bromides **4a**–**h** in refluxing dioxane in the presence of triethylamine afforded, in each case, one isolable product as evidenced by TLC analysis. On the basis of elemental analyses and MS, IR, and ^{1}H NMR the isolated products were assigned the structure of 5-amino-4-arylazo-3-methyl-1-(*N*-aryl-2-oxo-2-phenylethanehydrazonoyl)-pyrazole **5** (Scheme 1). The other isomeric structure **11** was discarded on the basis that reactions of 5-amino-3,4-disubstituted-pyrazoles with hydrazonoyl halides gave the respective amidrazones, which in some cases cyclize in situ to give 1*H*-3-arylazo-imidazo[1,2-*b*]pyrazole derivatives.[19,20]

Similarly, the hydrazonoyl bromide **4c** reacted with each of the compounds **3a**–**g** under the same conditions yielded one product in each case, which was assigned the structure of the amidrazones **6** (Scheme 1). On the basis of their microanalyses and spectroscopic data, the isolated products were identified as 5-amino-4-arylazo-3-methyl-1-(*N*-aryl 2-oxo-2-phenylethanehydrazonoyl)-pyrazoles **6** (Scheme 1).

Heating the amidrazones **5** and **6** each in acetic acid resulted in their dehydrative cyclization to afford the corresponding bis(arylazo) derivatives **8** and **9** (Scheme 1). Similar reaction of **3a** with **4a** under the same conditions afforded also the respective amidrazone **7a**, which cyclized also upon heating in acetic acid to afford **10a** (Scheme 1). However, reactions of **3a** with **4g** and that of **3g** with each of **4a** and **4g** were found to give the respective bis(arylazo)imidazopyrazole derivatives **10b**–**d** directly as end products (Scheme 1).

The IR spectra of the studied compounds **8**–**10** revealed the absence of the absorption bands due to CO and NH_2 groups present in the spectra of their precursors **5** and **6**. However, the spectra of **8**–**10** showed in each case, a characteristic NH band in the region 3200–3050 cm^{-1}. Their ^{1}H NMR spectra in DMSO exhibited a broad singlet signal centered at δ 10.0–11.3 due to the NH proton. Their mass spectra revealed in each case the respective molecular ion peak and the (M^++1) peak. Although such peaks were intense, they were not the base peaks. Their high relative intensities indicate that the molecular ions of the studied compounds are relatively stable. In addition the spectra showed characteristic peaks at *m*/*z* values corresponding to C_6H_5, XC_6H_4, and $C_{11}H_6N_3$ ion fragments. The latter fragment corresponds to either 2-phenyl- or 6-phenyl-1*H*-imidazo[1,2-*b*]pyrazole residue. Although the foregoing

Table 1
Electronic absorption spectra of compounds **8**–**10** in dioxane

Compd no.	λ_{max} (dioxane) (log ε)	Compd no.	λ_{max} (dioxane) (log ε)
8a	487 (3.76), 375 (3.69)	**9a**	488 (4.45), 326 (4.10)
8b	480 (3.64), 385 (3.83)	**9b**	490 (3.96), 325 (3.49)
8c[a]	487 (3.93), 385 (3.84)	**9d**	492 (4.00), 323 (3.56)
8d	490 (4.12), 390 (4.11)	**9e**	495 (3.99), 330 (4.34)
8e	492 (3.56), 378 (3.58)	**9f**	490 (3.66), 350 (3.95)
8f	485 (4.00), 395 (3.99)	**9g**	493 (3.95), 340 (3.76)
8g	470 (3.38), 369 (3.63)	**10a**	493 (4.16), 389 (4.10)
8h	487 (3.92), 380 (3.67)	**10b**	493 (4.16), 389 (4.10)
		10c	495 (4.10), 385 (4.07)
		10d	497 (4.07), 385 (4.22)

[a] Solvent: λ_{max} nm (log ε) ethanol: 478 (4.01); chloroform: 492 (4.15); acetic acid: 476 (3.35); pyridine: 475 (4.32); ether: 481 (4.02).

spectroscopic data are consistent with the assigned structures **8**–**10**, they cannot distinguish between the four possible tautomeric forms **A**–**D** (Fig. 1).

To elucidate the actual tautomeric form(s) of these compounds, their electronic absorption spectra were first studied. The spectra of the compounds in dioxane showed in each case two absorption bands in the regions 495–480 and 325–385 nm (Table 1). This absorption pattern is analogous to that reported for the azo chromophore.[21,22] Also, the electronic absorption spectra of **8c**, taken as a typical example of the three series prepared, in different solvents showed little, if any, shift (Table 1). This result indicates that the studied compounds exist in one tautomeric bis-arylazo form **A** or **D**.

To provide a conclusive evidence for the tautomeric structure of compounds **8**–**10**, their acid dissociation constants were determined by spectrophotometric method in 80% (v/v) dioxane/water mixture at 27 °C and an ionic strength of 0.1. From the pH-absorbance data, the p*K* values were calculated and the results are summarized in Tables 2–4. Correlation of these p*K* data with the Hammett substituent σ constant using the least squares method resulted in the following linear correlations:

$$pK(\mathbf{8a}–\mathbf{h}) = 10.228 - 1.685\sigma, \quad r^2 = 0.991; s = \pm 0.034$$

$$pK(\mathbf{9a}–\mathbf{g}) = 10.228 - 1.761\sigma, \quad r^2 = 0.992; \ s = \pm 0.061$$

$$pK(\mathbf{10a}–\mathbf{e}) = 10.220 - 1.712\sigma, \quad r^2 = 0.998; \ s = \pm 0.037$$

where *r* and *s* are the correlation coefficient and standard deviation. Correlation of the data for the three series together, gave the following linear equation:

$$pK(\mathbf{8}–\mathbf{10}) = 10.227 - 1.717\sigma, \quad r^2 = 0.993; \ s = \pm 0.045.$$

Table 2
Acid dissociation constant p*K* of compounds **8a**–**h**

Compd no.	σ	σ^-	p*K* ($\pm s$)	λ_{max}[a]	λ_{max}[b]	$\Delta\nu$ (cm^{-1})	p*K**
8a	−0.27	−0.27	10.71 (0.09)	455	526	2966	4.48
8b	−0.17	−0.17	10.44 (0.04)	453	524	2991	4.16
8c	0.00	0.00	10.25 (0.02)	452	531	3291	3.34
8d	0.23	0.23	9.87 (0.04)	447	532	3574	2.36
8e	0.37	0.37	9.64 (0.03)	445	533	3710	1.85
8f	0.71	0.71	9.12 (0.06)	444	542	4072	0.57
8g	0.78	1.28	8.82 (0.08)	465	585	4411	0.44
8h	0.45	0.68	9.44 (0.01)	454	549	3811	1.44

[a] In acid medium.
[b] In alkaline medium.

Table 3
Acid dissociation constant p*K* of compounds **9a–f**

Compd no.	σ	σ^-	p*K* (±*s*)	λ_{max}[a]	λ_{max}[b]	$\Delta\nu$ (cm^{-1})	p*K**
9a	−0.27	−0.27	10.63 (0.08)	450	525	3175	3.96
9b	−0.17	−0.17	10.48 (0.05)	448	527	3346	3.45
9c	0.00	0.00	10.25 (0.02)	452	531	3291	3.34
9d	0.23	0.23	9.91 (0.04)	444	427	3547	2.46
9e	0.37	0.37	9.71 (0.05)	446	530	3553	2.25
9f	0.71	0.71	9.01 (0.01)	450	540	3703	1.23
9g	0.78	1.28	8.70 (0.06)	456	552	3813	0.69

[a] In acid medium.
[b] In alkaline medium.

Such excellent linear correlations indicate that the studied compounds **8–10** exist predominantly in the 1*H*-tautomeric form namely the bis(arylazo)structure **A** (Fig. 1).This is because if they exist in one of the mixed azo-hydrazone tautomeric structure **B** or **C**, their p*K* values will be better correlated with the enhanced Hammett substituent constant σ^- rather than σ as in such tautomeric forms the substituent is in direct interaction with the negative charge on the acidic site ArN– or Ar′N–. However, this was not found to be the case. For example, correlation of the p*K* data with σ^- gave poor correlations as shown by the values of the correlation coefficients and standard deviation as shown below:

$$pK(\mathbf{8a}–\mathbf{h}) = 10.223 - 1.235\sigma^-, \quad r^2 = 0.957; \ s = \pm 0.117$$

$$pK(\mathbf{9a}–\mathbf{g}) = 10.219 - 1.322\sigma^-, \quad r^2 = 0.966; \ s = \pm 0.109$$

$$pK(\mathbf{10a}–\mathbf{e}) = 10.425 - 1.118\sigma^-, \quad r^2 = 0.992; \ s = \pm 0.121$$

$$pK(\mathbf{8}–\mathbf{10}) = 10.239 - 1.130\sigma^-, \quad r^2 = 0.953; \ s = \pm 0.163.$$

On the basis of this finding, both tautomeric forms **B** and **C** were discarded. Furthermore, if the compounds **8–10** had the 5*H*-structure namely the **D**-form (Fig. 1), the ρ value for series **8** will be much less than that for series **9**. This is because in structure **D** (Fig. 1), the bridge Ar′–N=N–C(3)=C(2)–N(1)=C(7a)–C(7)=C(6)– between the acidic site namely –N(5)H and the substituent in Ar′ group is longer than the bridge Ar–N=N–C(7)=C(6)– between the substituent and the same acidic site –N(5)H and the substituent in Ar group. Since this was not found to be the case, the tautomeric structure **D** (Fig. 1) was also discarded.

Next, we calculated the acidity constants p*K** of the three series **8–10** in their corresponding singlet excited states utilizing the so-called Forster energy-cycle.[23] According to this cycle, $pK^* = pK + 0.625(\Delta\nu)/T$, where p*K* and p*K** are the acid dissociation constants in the ground and the singlet excited states, respectively, and ($\Delta\nu$) represents the frequency difference in cm^{-1} between the values of absorption λ_{max} of the compound in acid and alkaline media.[24] The results of such calculations are summarized in Tables 2–4. Correlation of these p*K** data for the three series **8–10**, gave the following linear equations:

$$pK^*(\mathbf{8a}–\mathbf{h}) = 3.374 - 4.393\sigma, \quad r^2 = 0.987; \ s = \pm 0.048$$

$$pK^*(\mathbf{9a}–\mathbf{g}) = 3.172 - 2.695\sigma, \quad r^2 = 0.984; \ s = \pm 0.060$$

$$pK^*(\mathbf{10a}–\mathbf{e}) = 3.663 - 3.992\sigma, \quad r^2 = 0.918; \ s = \pm 0.026$$

$$pK^*(\mathbf{8}–\mathbf{10}) = 3.367 - 3.805\sigma, \quad r^2 = 0.923; \ s = \pm 0.046.$$

Such linear equations collectively indicate that the studied compounds exist in the bis-azo tautomeric form **A** in the excited state too. In addition, the larger values for ρ^* emphasize the importance of the electronic interactions in the excited state.[24]

In conclusion, hydrazonoyl halides are useful precursors for synthesis of the title bis(arylazo) dyes. The spectroscopic data of the compounds prepared and the correlation of their acidity constants with the Hammett equation have proved that such compounds exist predominantly in the 1*H*-bis-(arylazo) tautomeric form in both ground and excited states.

Table 4
Acid dissociation constant p*K* of compounds **10a–d**

Compd no.	$\sum\sigma$	$\sum\sigma^-$	p*K* (±*s*)	λ_{max}[a]	λ_{max}[b]	$\Delta\nu$ (cm^{-1})	p*K**
10a	−0.54	−0.54	11.16 (0.04)	452	520	2893	5.08
8c	0.00	0.00	10.25 (0.02)	452	531	3291	3.34
10b	0.51	1.01	9.37 (0.01)	440	515	3310	2.42
10c	0.51	1.01	9.25 (0.08)	458	533	3257	2.79
10d	1.56	2.56	7.58 (0.07)	448	586	3072	−3.46

[a] In acid medium.
[b] In alkaline medium.

3. Experimental

3.1. General

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded in potassium bromide using Perkin Elmer FTIR 1650 and Pye-Unicam SP300 infrared spectrophotometers. ^{1}H NMR spectra were recorded in deuterated dimethyl sulfoxide using a Varian Gemini 200 NMR spectrometer. Mass spectra were recorded on a GCMS-QP 1000 EX Shimadzu and GCMS 5988-A HP spectrometers. Electronic absorption spectra were recorded on Perkin–Elmer Lambada 40 spectrophotometer. Elemental analyses were carried out at the Microanalytical Laboratory of Cairo University, Giza, Egypt.

3-Iminobutyronitrile **1**,[16] 2-arylhydrazono-3-iminobutyronitriles **2**,[17] and *N*-Aryl 2-oxo-2-phenyethanehydrazonoyl bromides **4**[18a,b] were prepared as previously described.

3.2. 5-Amino-4-arylazo-3-methylpyrazoles 3a–g

General procedure. A solution of compound **2** (0.1 mol) and hydrazine hydrate (5.0 mL, 0.1 mol) in absolute ethanol (100 mL) was refluxed for 15 h then the solvent was evaporated under vacuum. The solid left was collected and crystallized from the appropriate solvent to give the respective compound **3**. The physical constants of the compounds prepared **3a–g** are given below.

*3.2.1. 5-Amino-4-(4-methoxyphenylazo)-3-methylpyrazole (**3a**)*
Yellow solid (19.9 g, 86%), mp 178–180 °C (EtOH); IR ν (KBr) 3467, 3355 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 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.

*3.2.2. 5-Amino-4-(4-methylphenylazo)-3-methylpyrazole (**3b**)*
Yellow solid (17.4 g, 81%), mp 177–178 °C, lit. 178 °C.[25]

*3.2.3. 5-Amino-4-(phenylazo)-3-methylpyrazole (**3c**)*
Yellow solid (16.5 g, 82%), mp 196–197 °C, lit. 198 °C.[26]

*3.2.4. 5-Amino-4-(4-chlorophenylazo)-3-methylpyrazole (**3d**)*

Yellow solid (18.8 g, 80%), mp 180–182 °C (EtOH); IR ν (KBr) 3410, 3298 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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.

*3.2.5. 5-Amino-4-(3-chlorophenylazo)-3-methylpyrazole (**3e**)*

Yellow solid (19.5 g, 83%), mp 168–170 °C (EtOH); IR ν (KBr) 3402, 3294 cm^{-1}; ^1H NMR (DMSO-d_6) δ 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.

*3.2.6. 5-Amino-3-methyl-4-(3-nitrophenylazo)-pyrazole (**3f**)*

Yellow solid (20.0 g, 82%), mp 210–212 °C (EtOH); IR ν (KBr) 3456, 3348 cm^{-1}; ^1H NMR (DMSO-d_6) δ 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 $C_{10}H_{10}N_6O_2$ (246.00): C, 48.78; H, 4.09; N, 34.13. Found: C, 48.33; H, 3.64; N, 34.05.

*3.2.7. 5-Amino-3-methyl-4-(4-nitrophenylazo)-pyrazole (**3g**)*

Yellow solid (19.6 g, 80%), mp 150–152 °C (EtOH); IR ν (KBr) 3483, 3363 cm^{-1}; ^1H NMR (DMSO-d_6) δ 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 $C_{10}H_{10}N_6O_2$ (246.00): C, 48.78; H, 4.09; N, 34.13. Found: C, 48.62; H, 3.91; N, 33.84.

3.3. 5-Amino-4-arylazo-1-(*N*-aryl-2-oxo-2-phenylethanehydrazonoyl)-3-methyl-pyrazoles (5, 6, and 7a)

General procedure. To a mixture of the aminopyrazole derivative **3c** (5 mmol) and the appropriate hydrazonoyl bromide **4** (5 mmol) in dioxane (20 mL), triethylamine (0.7 mL) was added. The reaction mixture was refluxed for 10 h. The solvent was evaporated under vacuum. The solid left was collected and crystallized from the appropriate solvent to give compounds **5**.

Repetition of the above procedure using **4c** and the appropriate aminopyrazole **3** afforded the respective compounds **6**.

Reactions of **3a** with **4a** and that of **3a** with **4g** and of **3g** with each of **4a** and **4g** when they were carried out following the above procedure afforded the respective **7a** and the imidazopyrazole derivatives **10b–d**, respectively.

The physical constants of the compounds **5a–h**, **6a–g**, **7a**, and **10b–d** are listed below.

*3.3.1. 5-Amino-4-(phenylazo)-1-[N-(4-methoxyphenyl)-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**5a**)*

Yellow solid (1.36 g, 60%), mp 280–282 °C (dioxane); IR ν (KBr) 3363, 3193, 1743 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.43 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 6.82 (s, 2H, NH_2), 7.24–7.64 (m, 10H, ArH), 7.78 (d, J=9 Hz, 2H, ArH), 7.99 (d, J=9 Hz, 2H, ArH), 11.05 (s, 1H, NH); MS m/z (%) 454 (M^++1, 19), 453 (M^+, 24), 253 (8), 201 (2), 121 (17), 106 (9), 105 (100), 77 (43). Anal. Calcd for $C_{25}H_{23}N_7O_2$ (453.51): C, 66.21; H, 5.11; N, 21.62. Found: C, 66.99; H, 4.94; N, 21.50.

*3.3.2. 5-Amino-4-(phenylazo)-1-[N-(4-methylphenyl)-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**5b**)*

Yellow solid (1.42 g, 65%), mp 230–232 °C (dioxane); IR ν (KBr) 3440, 3178, 1743 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.36 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.80 (s, 2H, NH_2), 7.31–7.64 (m, 10H, ArH), 7.74 (d, J=8 Hz, 2H, ArH), 7.99 (d, J=8 Hz, 2H, ArH), 11.10 (s, 1H, NH); MS m/z (%) 438 (M^++2, 16), 437 (M^+, 16), 422 (6), 420 (8), 237 (2), 106 (11), 105 (100), 91 (9), 77 (43). Anal. Calcd for $C_{25}H_{23}N_7O$ (437.51): C, 68.63; H, 5.30; N, 22.41. Found: C, 68.60; H, 4.90; N, 22.10.

*3.3.3. 5-Amino-4-(phenylazo)-1-[N-phenyl-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**5c**)*

Yellow solid (1.52 g, 72%), mp 240–242 °C (dioxane); IR ν (KBr) 3298, 3186, 1701 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.62 (s, 3H, CH_3), 6.52 (s, 2H, NH_2), 7.05–8.09 (m, 15H, ArH), 10.98 (s, 1H, NH); MS m/z (%) 425 (M^++2, 6), 424 (M^++1, 22), 423 (M^+, 18), 407 (24), 329 (15), 288 (13), 201 (21), 124 (23), 105 (92), 91 (13), 77 (100). Anal. Calcd for $C_{24}H_{21}N_7O$ (423.48): C, 68.07; H, 5.00; N, 23.15. Found: C, 67.80; H, 4.70; N, 23.10.

*3.3.4. 5-Amino-4-(phenylazo)-1-[N-(4-chlorophenyl)-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**5d**)*

Brown solid (1.60 g, 70%), mp 228–230 °C (dioxane); IR ν (KBr) 3300, 3217, 1700 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.60 (s, 3H, CH_3), 6.50 (s, 2H, NH_2), 7.03–7.56 (m, 10H, ArH), 7.73 (d, J=10 Hz, 2H, ArH), 8.02 (d, J=10 Hz, 2H, ArH), 11.0 (s, 1H, NH); MS m/z (%) 459 (M^++2, 9), 458 (M^++1, 17), 457 (M^+, 22), 441 (11), 440 (13), 439 (17), 201 (40), 124 (32), 105 (100), 91 (7), 77 (81). Anal. Calcd for $C_{24}H_{20}ClN_7O$ (457.93): C, 62.95; H, 4.40; N, 21.41. Found: C, 62.80; H, 4.10; N, 21.20.

*3.3.5. 5-Amino-4-(phenylazo)-1-[N-(3-chlorophenyl)-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**5e**)*

Yellow solid (1.58 g, 69%), mp 218–220 °C (DMF); IR ν (KBr) 3300, 3200, 1743 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.42 (s, 3H, CH_3), 6.79 (s, 2H, NH_2), 7.08–8.03 (m, 14H, ArH), 11.16 (s, 1H, NH); MS m/z (%) 459 (M^++2, 7), 458 (M^++1, 16), 457 (M^+, 22), 440 (24), 439 (36), 362 (16), 288 (13), 201 (41), 180 (15), 124 (37), 111 (12), 105 (82), 91 (13), 77 (100). Anal. Calcd for $C_{24}H_{20}ClN_7O$ (457.93): C, 62.95; H, 4.40; N, 21.41. Found: C, 63.30; H, 4.40; N, 21.60.

*3.3.6. 5-Amino-4-(phenylazo)-1-[N-(3-nitrophenyl)-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**5f**)*

Brown solid (1.60 g, 68%), mp 240–242 °C (dioxane/methanol); IR ν (KBr) 3355, 3206, 1679 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.36 (s, 3H, CH_3), 6.80 (s, 2H, NH_2), 7.31–8.01 (m, 14H, ArH), 11.06 (s, 1H, NH); MS m/z (%) 469 (M^++1, 18), 468 (M^+, 12), 451 (30), 450 (49), 252 (14), 201 (25), 180 (30), 122 (10), 115 (16), 105 (52), 91 (21), 77 (100). Anal. Calcd for $C_{24}H_{20}N_8O_3$ (468.48): C, 61.53; H, 4.29; N, 23.92. Found: C, 61.20; H, 4.50; N, 24.10.

*3.3.7. 5-Amino-4-(phenylazo)-1-[N-(4-nitrophenyl)-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**5g**)*

Brown solid (1.71 g, 73%), mp 254–256 °C (dioxane); IR ν (KBr) 3380, 3217, 1720 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.60 (s, 3H, CH_3), 6.45 (s, 2H, NH_2), 7.00–7.60 (m, 10H, ArH), 7.70 (d, J=9 Hz, 2H, ArH), 8.00 (d, J=9 Hz, 2H, ArH), 11.20 (s, 1H, NH); MS m/z (%) 469 (M^++1, 13), 468 (M^+, 14), 451 (45), 373 (30), 288 (17), 252 (16), 201 (26), 180 (31), 124 (29), 115 (15), 105 (65), 91 (22), 77 (100). Anal. Calcd for $C_{24}H_{20}N_8O_3$ (468.48): C, 61.53; H, 4.29; N, 23.92. Found: C, 61.10; H, 4.10; N, 23.80.

*3.3.8. 5-Amino-4-(phenylazo)-1-[N-(4-ethylcarboxylatephenyl)-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**5h**)*

Brown solid (1.81 g, 73%), mp 140–142 °C (dioxane); IR ν (KBr) 3440, 3220, 1705, 1680 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.16 (t, J=7 Hz, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.28 (q, J=7 Hz, 2H, CH_2), 6.35 (s, 2H, NH_2), 7.39–7.69 (m, 10H, ArH), 7.77 (d, J=9 Hz, 2H, ArH), 8.01 (d, J=9 Hz, 2H, ArH), 11.30 (s, 1H, NH); MS m/z (%) 496 (M^++1, 5), 495 (M^+, 3), 478 (100), 400 (58), 344 (15), 288 (57), 209 (18), 180 (48), 149 (9), 105 (38), 91 (24), 77 (73). Anal. Calcd for $C_{27}H_{25}N_7O_3$ (495.0): C, 65.44; H, 5.09; N, 19.79. Found: C, 65.60; H, 4.70; N, 19.60.

*3.3.9. 5-Amino-4-(4-methoxyphenylazo)-1-[N-phenyl-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**6a**)*

Yellow solid (1.94 g, 86%), mp 212–214 °C (dioxane); IR ν (KBr) 3402, 3298, 1639 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.40 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 6.40 (s, 2H, NH_2), 7.20–7.90 (m, 10H, ArH), 6.80 (d, J=7 Hz, 2H, ArH), 7.00 (d, J=7 Hz, 2H, ArH), 11.03 (s, 1H, NH); MS m/z (%) 454 (M^++1, 3), 453 (M^+, 11), 231 (59), 124 (39), 121 (19), 107 (13), 105 (100), 92 (13), 77 (94). Anal. Calcd for $C_{25}H_{23}N_7O_2$ (453.51): C, 66.21; H, 5.11; N, 21.62. Found: C, 66.02; H, 5.00; N, 20.42.

*3.3.10. 5-Amino-4-(4-methylphenylazo)-1-[N-phenyl-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**6b**)*

Yellow solid (1.84 g, 84%), mp 206–208 °C (EtOH); IR ν (KBr) 3390, 3286, 1639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H, CH_3), 2.61 (s, 3H, CH_3), 6.25 (s, 2H, NH_2), 7.03–7.09 and 7.25–7.66 (m, 10H, ArH), 7.12 (d, J=7 Hz, 2H, ArH), 8.05 (d, J=7 Hz, 2H, ArH), 10.99 (s, 1H, NH); MS m/z (%) 438 (M^++1, 17), 437 (M^+, 2), 421(14), 215 (45), 124 (37), 105 (100), 91 (23), 77 (78). Anal. Calcd for $C_{25}H_{23}N_7O$ (437.51): C, 68.63; H, 5.30; N, 22.41. Found: C, 68.25; H, 5.00; N, 22.30.

*3.3.11. 5-Amino-4-(4-chlorophenylazo)-1-[N-phenyl-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**6d**)*

Yellow solid (1.81 g, 79%), mp 210–212 °C (dioxane); IR ν (KBr) 3367, 3267, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60 (s, 3H, CH_3), 6.50 (s, 2H, NH_2), 7.12–7.90 (m, 10H, ArH), 7.09 (d, J=7 Hz, 2H, ArH), 8.04 (d, J=7 Hz, 2H, ArH), 10.93 (s, 1H, NH); MS m/z (%) 459 (M^++2, 3), 458 (M^++1, 2), 457 (M^+, 7), 439 (18), 328 (16), 322 (11), 214 (11), 105 (100), 77 (91). Anal. Calcd for $C_{24}H_{20}ClN_7O$ (457.93): C, 62.95; H, 4.40; N, 21.41. Found: C, 62.73; H, 4.05; N, 21.34.

*3.3.12. 5-Amino-4-(3-chlorophenylazo)-1-[N-phenyl-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**6e**)*

Orange solid (1.55 g, 68%), mp 186–188 °C (dioxane); IR ν (KBr) 3379, 3274, 1643 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.42 (s, 3H, CH_3), 6.78 (s, 2H, NH_2), 7.31–8.03 (m, 14H, ArH), 11.04 (s, 1H, NH); MS m/z (%) 459 (M^++2, 1), 458 (M^++1, 1), 457 (M^+, 3), 214 (4), 124 (11), 111 (9), 105 (100), 91 (3), 77 (56). Anal. Calcd for $C_{24}H_{20}ClN_7O$ (457.93): C, 62.95; H, 4.40; N, 21.41. Found: C, 62.63; H, 3.98; N, 21.00.

*3.3.13. 5-Amino-4-(3-nitrophenylazo)-1-[N-phenyl-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**6f**)*

Brown solid (1.59 g, 68%), mp 238–240 °C (EtOH); IR ν (KBr) 3363, 3232, 1705 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.42 (s, 3H, CH_3), 7.00 (s, 2H, NH_2), 7.31–8.56 (m, 14H, ArH), 11.10 (s, 1H, NH); MS m/z (%) 469 (M^++1, 4), 468 (M^+, 7), 450 (34), 328 (28), 287 (16), 105 (97), 77 (100). Anal. Calcd for $C_{24}H_{20}N_8O_3$ (468.48): C, 61.53; H, 4.29; N, 23.92. Found: C, 61.15; H, 4.35; N, 23.80.

*3.3.14. 5-Amino-4-(4-nitrophenylazo)-1-[N-phenyl-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**6g**)*

Dark red solid (1.40 g, 60%), mp 198–200 °C (dioxane); IR ν (KBr) 3350, 3201, 1666 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.45 (s, 3H, CH_3), 6.40 (s, 2H, NH_2), 7.00–7.80 (m, 10H, ArH), 7.85 (d, J=7 Hz, 2H, ArH), 8.40 (d, J=7 Hz, 2H, ArH), 11.00 (s, 1H, NH); MS m/z (%) 469 (M^++1, 3.5), 468 (M^+, 20), 424 (30), 218 (14), 179 (33), 122 (1.8), 117 (8.8), 105 (36), 91 (54), 77 (100). Anal. Calcd for $C_{24}H_{20}N_8O_3$ (468.48): C, 61.53; H, 4.29; N, 23.92. Found: C, 61.31; H, 4.50; N, 23.81.

*3.3.15. 5-Amino-4-(4-methoxyphenylazo)-1-[N-(4-methoxyphenyl)-2-oxo-2-phenylethanehydrazonoyl]-3-methyl-pyrazole (**7a**)*

Brown solid (1.9 g, 82%), mp 220–222 °C (dioxane); IR ν (KBr) 3433, 3236, 1655 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.39 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.20 (s, 2H, NH_2), 6.90 (d, J=8 Hz, 2H, ArH), 7.01 (d, J=9 Hz, 2H, ArH), 7.22–7.56 (m, 5H, ArH), 7.70 (d, J=8 Hz, 2H, ArH), 7.96 (d, J=8 Hz, 2H, ArH), 10.96 (s, 1H, NH); MS m/z (%) 484 (M^++1, 23), 483 (M^+, 34), 466 (32), 231 (24), 121 (21), 107 (17), 105 (100), 77 (46). Anal. Calcd for $C_{26}H_{25}N_7O3$ (483.53): C, 64.58; H, 5.21; N, 20.28. Found: C, 64.23; H, 4.90; N, 20.12.

*3.3.16. 3-(4-Methoxyphenylazo)-7-(4-nitrophenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**10b**)*

Brown solid (1.8 g, 76%), mp 160–162 °C (AcOH); IR ν (KBr) 3200 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.62 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 7.38–7.41 (m, 5H, ArH), 7.53 (d, J=7 Hz, 2H, ArH), 7.58 (d, J=8 Hz, 2H, ArH), 8.16 (d, J=7 Hz, 2H, ArH), 8.50 (d, J=8 Hz, 2H, ArH), 11.20 (s, 1H, NH); MS m/z (%) 482 (M^++2, 1), 480 (M^+, 4), 320 (11), 288 (59), 246 (19), 166 (51), 138 (21), 124 (66), 105 (100), 77 (80). Anal. Calcd for $C_{25}H_{20}N_8O_3$ (480.49): C, 62.49; H, 4.20; N, 23.32. Found: C, 62.22; H, 4.10; N, 23.22.

*3.3.17. 3-(4-Nitrophenylazo)-7-(4-methoxyphenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**10c**)*

Brown solid (1.7 g, 72%), mp 234–236 °C (AcOH); IR ν (KBr) 3200 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.72 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 7.10 (d, J=9 Hz, 2H, ArH), 7.38–7.41 (m, 5H, ArH), 7.63(d, J=6 Hz, 2H, ArH), 7.83 (d, J=9 Hz, 2H, ArH), 8.29 (d, J=6 Hz, 2H, ArH), 10.65 (s, 1H, NH); MS m/z (%) 481 (M^++1, 37), 480 (M^+, 32), 210 (33), 209 (17), 121 (62), 115 (25), 107 (50), 105 (26), 91 (12), 77 (100). Anal. Calcd for $C_{25}H_{20}N_8O_3$ (480.49): C, 62.49; H, 4.20; N, 23.32. Found: C, 62.15; H, 4.02; N, 22.51.

*3.3.18. 3,7-Bis(4-nitrophenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**10d**)*

Dark red solid (1.9 g, 80%), mp 238–240 °C (dioxane); IR ν (KBr) 3271 cm^{-1}; ^1H NMR (TFAA) δ 2.77 (s, 3H, CH_3), 7.64 (d, J=8 Hz, 2H, ArH), 7.87 (d, J=9 Hz, 2H, ArH), 7.91 (d, J=8 Hz, 2H, ArH), 7.93–8.08 (m, 5H, ArH), 8.32 (d, J=9 Hz, 2H, ArH), 10.83 (s, 1H, NH); MS m/z (%) 497 (M^++2, 2), 496 (M^++1, 7), 495 (M^+, 4), 251 (10), 246 (17), 225 (11), 138 (19), 124 (24), 122 (11), 105 (100), 92 (13), 77 (75). Anal. Calcd for $C_{24}H_{17}N_9O_4$ (495.46): C, 58.18; H, 3.46; N, 25.44. Found: C, 58.34; H, 3.21; N, 24.62.

3.4. 3,7-Bis(arylazo)-6-methyl-2-phenyl-1*H*-imidazo[1,2-*b*]-pyrazoles (8, 9, and 10a)

General procedure. A solution of the appropriate **5**, **6** or **7a** (2 mmol) in glacial acetic acid (25 mL) was refluxed for 5 h and the solvent was then evaporated. The residue left was triturated with water. The precipitated solid was collected by filtration, washed with water, and crystallized from suitable solvent to yield the respective compounds **8**, **9**, and **10a**. Their physical constants are listed below.

*3.4.1. 3-(4-Methoxyphenylazo)-7-phenylazo-6-methyl-2-phenyl-1H-imidazo-[1,2-b]pyrazole (**8a**)*

Brown solid (0.6 g, 66%), mp 190–192 °C (AcOH); IR ν (KBr) 3440 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.57 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 7.39–7.61 (m, 10H, ArH), 7.69 (d, J=9 Hz, 2H, ArH), 8.31 (d, J=9 Hz, 2H, ArH), 11.0 (s, 1H, NH); MS m/z (%) 436 (M^++1, 53), 435 (M^+, 5), 328 (1), 172 (6), 157 (2), 105 (100), 91 (15), 77 (82). Anal. Calcd for $C_{25}H_{21}N_7O$ (435.49): C, 68.95; H, 4.86; N, 22.51. Found: C, 69.10; H, 4.80; N, 22.20.

*3.4.2. 3-(4-Methylphenylazo)-7-phenylazo-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**8b**)*

Brown solid (0.52 g, 62%), mp 168–170 °C (AcOH); IR ν (KBr) 3425 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.66 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 7.25–7.71 (m, 10H, ArH), 8.11 (d, J=9 Hz, 2H, ArH), 8.34 (d, J=9 Hz, 2H, ArH), 11.30 (s, 1H, NH); MS m/z (%) 420 (M^++1, 85), 419 (M^+, 29), 343 (17), 288 (13), 105 (96), 91 (46), 77 (100). Anal. Calcd

for $C_{25}H_{21}N_7$ (419.49): C, 71.58; H, 5.05; N, 23.37. Found: C, 71.60; H, 4.80; N, 23.0.

*3.4.3. 3,7-Bis(phenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b]-pyrazole (**8c**)*

Dark red solid (0.50 g, 62%), mp 220–222 °C (AcOH); IR ν (KBr) 3302 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.41 (s, 3H, CH_3), 7.48–8.33 (m, 15H, ArH), 11.0 (s, 1H, NH); MS *m*/*z* (%) 406 (M^++1, 36), 405 (M^+, 4), 243 (22), 228 (14), 166 (15), 124 (14), 105 (85), 91 (19), 77 (100). Anal. Calcd for $C_{24}H_{19}N_7$ (405.30): C, 71.10; H, 4.72; N, 24.18. Found: C, 71.03; H, 4.67; N, 23.90.

*3.4.4. 3-(4-Chlorophenylazo)-7-phenylazo-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**8d**)*

Brown solid (0.54 g, 61% yield), mp 184–186 °C (AcOH); IR ν (KBr) 3417 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.36 (s, 3H, CH_3), 7.31–7.65 (m, 10H, ArH), 7.74 (d, *J*=9 Hz, 2H, ArH), 7.99 (d, *J*=9 Hz, 2H, ArH), 11.10 (s, 1H, NH); MS *m*/*z* (%) 442 (M^++2, 16), 441 (M^++1, 15), 440 (M^+, 40), 439 (11), 362 (28), 334 (14), 306 (12), 288 (42), 209 (13), 180 (45), 115 (18), 111 (44), 91 (24), 77 (100). Anal. Calcd for $C_{24}H_{18}ClN_7$ (439.91): C, 65.53; H, 4.12; N, 22.30. Found: C, 65.20; H, 4.00; N, 22.00.

*3.4.5. 3-(3-Chlorophenylazo)-7-phenylazo-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**8e**)*

Brown solid (0.57 g, 65%), mp 190–192 °C (AcOH); IR ν (KBr) 3260 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.69 (s, 3H, CH_3), 7.51–8.33 (m, 14H, ArH), 10.90 (s, 1H, NH); MS *m*/*z* (%) 442 (M^++2, 27), 441 (M^++1, 30), 440 (M^+, 61), 439 (16), 364 (16), 362 (42), 288 (38), 242 (10), 180 (47), 115 (20), 111 (30), 105 (27), 91 (30), 77 (100). Anal. Calcd for $C_{24}H_{18}ClN_7$ (439.91): C, 65.53; H, 4.12; N, 22.29. Found: C, 65.30; H, 3.90; N, 22.40.

*3.4.6. 3-(3-Nitrophenylazo)-7-phenylazo-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**8f**)*

Brown solid (0.56 g, 62%), mp 176–178 °C (AcOH); IR ν (KBr) 3240 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.66 (s, 3H, CH_3), 7.53–8.37 (m, 14H, ArH), 10.80 (s, 1H, NH); MS *m*/*z* (%) 451 (M^++1, 29), 450 (M^+, 100), 373 (58), 288 (31), 253 (15), 209 (12), 180 (49), 122 (12), 105 (24), 91 (26), 77 (81). Anal. Calcd for $C_{24}H_{18}N_8O_2$ (450.46): C, 63.99; H, 4.03; N, 24.88. Found: C, 63.80; H, 3.90; N, 24.60.

*3.4.7. 3-(4-Nitrophenylazo)-7-phenylazo-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**8g**)*

Dark green solid (0.63 g, 70%), mp 266–268 °C (AcOH); IR ν (KBr) 3270 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.49 (s, 3H, CH_3), 7.66–7.70 (m, 10H, ArH), 7.80 (d, *J*=9 Hz, 2H, ArH), 8.31 (d, *J*=9 Hz, 2H, ArH), 11.10 (s, 1H, NH); MS *m*/*z* (%) 451 (M^++1, 64), 450 (M^+, 33), 374 (42), 294 (14), 289 (27), 253 (17), 180 (47), 115 (24), 105 (19), 91 (32), 77 (100). Anal. Calcd for $C_{24}H_{18}N_8O_2$ (450.46): C, 63.99; H, 4.03; N, 24.88. Found: C, 64.00; H, 3.80; N, 24.70.

*3.4.8. 3-(4-Ethylcarboxylatephenylazo)-7-phenylazo-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**8h**)*

Brown solid (0.62 g, 65%), mp 180–182 °C (AcOH); IR ν (KBr) 3436, 1712 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.34 (t, *J*=8 Hz, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.32 (q, *J*=8 Hz, 2H, CH_2), 7.54–7.67 and 8.17–8.33 (m, 10H, ArH), 7.81 (d, *J*=8 Hz, 2H, ArH), 8.41 (d, *J*=8 Hz, 2H, ArH), 11.22 (s, 1H, NH); MS *m*/*z* (%) 478 (M^++1, 74), 477 (M^+, 6), 401 (20), 288 (17), 180 (13), 105 (100), 91 (27), 77 (95). Anal. Calcd for $C_{27}H_{23}N_7O_2$ (477.53): C, 67.91; H, 4.85; N, 20.53. Found: C, 67.80; H, 5.00; N, 20.20.

*3.4.9. 3-Phenylazo-7-(4-methoxyphenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**9a**)*

Dark red solid (0.50 g, 62%), mp 168–170 °C (AcOH); IR ν (KBr) 3398 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.32 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 7.56–7.59 and 8.32–8.34 (m, 10H, ArH), 7.08 (d, *J*=8 Hz, 2H, ArH), 7.80 (d, *J*=8 Hz, 2H, ArH), 11.0 (s, 1H, NH); MS *m*/*z* (%) 436 (M^++1, 41), 435 (M^+, 2), 149 (19), 135 (10), 123 (11), 111 (14), 104 (65), 92 (16), 77 (100). Anal. Calcd for $C_{25}H_{21}N_7O$ (435.49): C, 68.95; H, 4.86; N, 22.51. Found: C, 68.70; H, 4.61; N, 22.30.

*3.4.10. 3-Phenylazo-7-(4-methylphenylazo)-6-methyl-2-phenyl-1H-imidazo [1,2-b]pyrazole (**9b**)*

Dark red solid (0.50 g, 64%), mp 198–200 °C (AcOH); IR ν (KBr) 3382 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.04 (s, 3H, CH_3), 2.96 (s, 3H, CH_3), 7.23–7.71 (m, 10H, ArH), 8.06 (d, *J*=7 Hz, 2H, ArH), 8.46 (d, *J*=7 Hz, 2H, ArH), 11.25 (s, 1H, NH); MS *m*/*z* (%) 420 (M^++1, 14), 419 (M^+, 3), 198 (1), 105 (100), 104 (12), 91 (33), 77 (87). Anal. Calcd for $C_{25}H_{21}N_7$ (419.49): C, 71.58; H, 5.05; N, 23.37. Found: C, 71.32; H, 5.20; N, 23.30.

*3.4.11. 3-Phenylazo-7-(4-chlorophenylazo)-6-methyl-2-phenyl-1H-imidazo [1,2-b]pyrazole (**9d**)*

Brown solid (0.50 g, 65%), mp 280–282 °C (AcOH); IR ν (KBr) 3429 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 (s, 3H, CH_3), 7.28–7.85 (m, 10H, ArH), 7.95 (d, *J*=9 Hz, 2H, ArH), 8.21 (d, *J*=9 Hz, 2H, ArH), 11.25 (s, 1H, NH); MS *m*/*z* (%) 439 (M^+, 5), 353 (10), 227 (11), 179 (17), 139 (10), 118 (11), 110 (12), 105 (76), 91 (12), 77 (100). Anal. Calcd for $C_{24}H_{18}ClN_7$ (439.91): C, 65.53; H, 4.12; N, 22.30. Found: C, 65.25; H, 4.00; N, 22.15.

*3.4.12. 3-Phenylazo-7-(3-chlorophenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**9e**)*

Brown solid (0.50 g, 60%), mp 190–192 °C (AcOH); IR ν (KBr) 3382 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.60 (s, 3H, CH_3), 7.42–8.32 (m, 14H, ArH), 10.05 (s, 1H, NH); MS *m*/*z* (%) 442 (M^++2, 4), 441 (M^++1, 4), 440 (M^+, 13), 260 (2), 214 (1), 142 (3), 115 (1), 113 (4), 105 (100), 91 (2), 77 (88). Anal. Calcd for $C_{24}H_{18}ClN_7$ (439.91): C, 65.53; H, 4.12; N, 22.30. Found: C, 65.32; H, 4.04; N, 22.23.

*3.4.13. 3-Phenylazo-7-(3-nitrophenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**9f**)*

Brown solid (0.50 g, 66%), mp 240–242 °C (AcOH); IR ν (KBr) 3398 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.61 (s, 3H, CH_3), 7.34–8.48 (m, 14H, ArH), 9.65 (s, 1H, NH); MS *m*/*z* (%) 453 (M^++3, 10), 452 (M^++2, 47), 450 (M^+, 92), 333 (100), 287 (34), 272 (25), 196 (14), 179 (18), 115 (16), 91 (14), 77 (76). Anal. Calcd for $C_{24}H_{18}N_8O_2$ (450.46): C, 63.99; H, 4.03; N, 24.88. Found: C, 63.67; H, 3.88; N, 24.62.

*3.4.14. 3-Phenylazo-7-(4-nitrophenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b]pyrazole (**9g**)*

Brown solid (0.60 g, 70%), mp 210–212 °C (AcOH); IR ν (KBr) 3305 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.49 (s, 3H, CH_3), 6.89 (d, *J*=8 Hz, 2H, ArH), 7.38–7.77 and 7.80–7.95 (m, 10H, ArH), 7.77 (d, *J*=8 Hz, 2H, ArH), 11.20 (s, 1H, NH); MS *m*/*z* (%) 452 (M^++2, 50), 451 (M^++1, 100), 329 (18), 105 (57), 92 (13), 77 (84). Anal. Calcd for $C_{24}H_{18}N_8O_2$ (450.46): C, 63.99; H, 4.03; N, 24.88. Found: C, 63.86; H, 3.76; N, 24.80.

*3.4.15. 3,7-Bis(4-Methoxyphenylazo)-6-methyl-2-phenyl-1H-imidazo[1,2-b] pyrazole (**10a**)*

Brown solid (1.7 g, 80%), mp 180–182 °C (AcOH); IR ν (KBr) 3224 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.68 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 7.03 (d, *J*=8 Hz, 2H, ArH), 7.14 (d, *J*=9 Hz, 2H, ArH), 7.46 (d, *J*=9 Hz, 2H, ArH), 7.58–7.85 (m, 5H, ArH), 8.30 (d, *J*=8 Hz, 2H, ArH), 11.25 (s, 1H, NH); MS *m*/*z* (%) 467 (M^++2, 18), 466 (M^++1, 58), 465 (M^+, 7), 451 (13), 369 (19), 121 (42), 107 (29), 105 (81), 92 (17), 77 (100). Anal. Calcd for $C_{26}H_{23}N_7O_2$ (465.52): C, 67.08; H, 4.98; N, 21.06. Found: C, 67.50; H, 4.61; N, 2.31.

3.5. pK Determination

The acid dissociation constants p*K* values of the compounds **4** and **5** were determined spectrophotometrically in 80% (v/v) dioxane/water mixture at 27 °C and ionic strength of 0.01. An Orion 420 A pH meter fitted with combined glass electrode type 518635 was employed for measurement of pH values. The instrument was accurate to 0.01 pH unit. It was calibrated using two standard Beckman buffer solutions of pH 4.01 and 7.00. The pH meter readings (*B*) recorded in dioxane/water solutions were converted to hydrogen ion concentration [H^+] by means of the widely used relation of Van Uitert and Hass[27] 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 was determined by recording the pH values for a series of hydrochloric acid and sodium chloride such that the ionic strength is 0.1 in 80% (v/v) dioxane/water at 27 °C. The value of $\log U_H$ was found to be −0.48. The experimental procedure followed in the determination of p*K* constants and their calculations from the absorbance-pH data are as previously described.[28] The p*K* values were reproducible to ±0.02 p*K* unit. The results are given in Tables 2–4.

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