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

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Abstract—Two series of novel 3,7-bis(arylazo)-2,6-diphenyl-1*H*-imidazo[1,2-*b*]pyrazoles were prepared starting from *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides. The acid dissociation constants in both the ground and excited states, p*K* and p*K**, respectively, were determined for both series and were correlated by the Hammett equation. The results of such correlations together with spectral data indicated that the title compounds exist predominantly in the 1*H*-bis-(arylazo) form in both ground and excited states. © 2002 Published by Elsevier Science Ltd.

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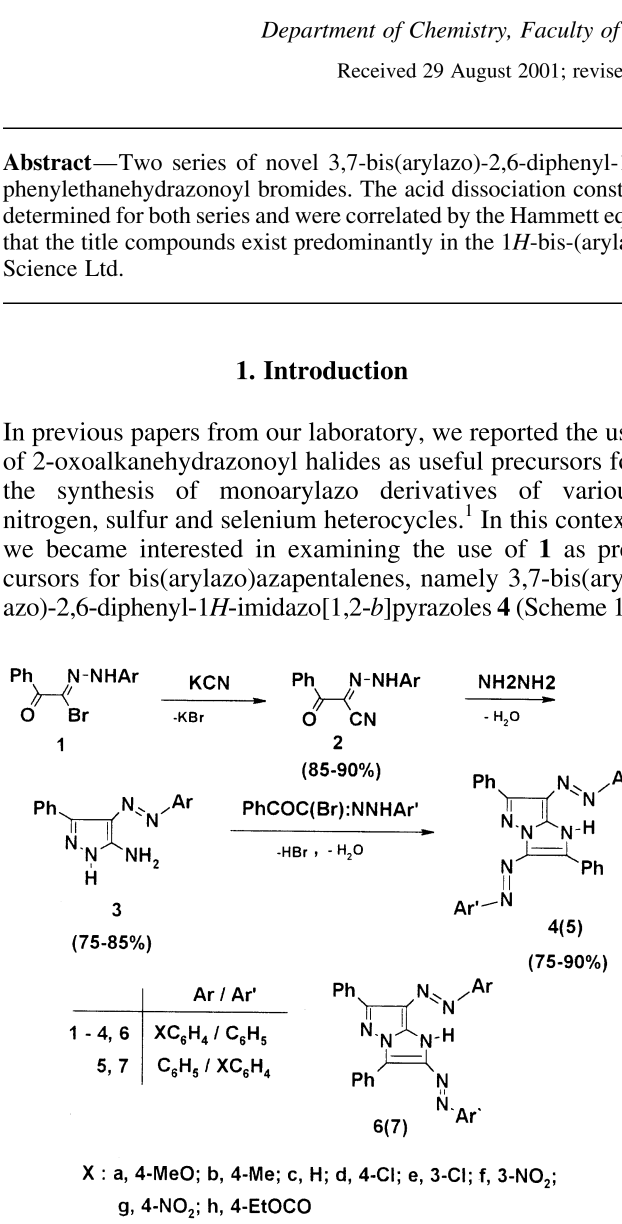
1. Introduction

In previous papers from our laboratory, we reported the use of 2-oxoalkanehydrazonoyl halides as useful precursors for the synthesis of monoarylazo derivatives of various nitrogen, sulfur and selenium heterocycles.[1] In this context, we became interested in examining the use of **1** as precursors for bis(arylazo)azapentalenes, namely 3,7-bis(arylazo)-2,6-diphenyl-1*H*-imidazo[1,2-*b*]pyrazoles **4** (Scheme 1).



Scheme 1.

To the best of our knowledge there have been no reports hitherto on the synthesis of the latter derivatives. The interest in such compounds is due to the fact that derivatives of azapentalene ring system are useful both in the field of material sciences and theoretical chemistry due to their unusual electronic features and physical properties.[2] For example, various derivatives of 1*H*-imidazo[1,2-*b*]pyrazole ring system have been recently reported to have potential utility as magenta photographic couplers[3–7] and as chromogenic redox indicators,[8] others have found uses as herbicides,[9] anti-inflammatory and anti-allergy[10,11] and anticancer agents against trypanosoma eruzil.[4,12] Thus, from a structure–activity viewpoint, the introduction of one or two arylazo groups into the azapentalene ring system may provide derivatives with increased or new utility. The strategy adopted herein for synthesis of the target compounds **4** is based on the use of *N*-aryl 2-oxo-2-phenylethanehydrazonoyl bromides **1** for the synthesis of arylazopyrazole derivative **3** that preserves a degree of functionality for building up another heterocyclic ring with another arylazo group as depicted in Scheme 1. Furthermore, it was thought interesting to elucidate the actual tautomeric structure of the compounds in question (Fig. 1) prior to investigating their biological activities.

2. Results and discussion

The required hydrazonoyl bromides **1** were prepared and converted into 2-arylhydrazono-3-oxo-3-phenylpropanenitriles **2** as previously reported from our laboratory[13] (Scheme 1). Treatment of the latter with hydrazine hydrate in refluxing ethanol afforded the respective 5-amino-4-arylzo-3-phenylpyrazoles **3** in good yields (Scheme 1).[14,15]

Keywords: acidity; azo compounds; imidazoles; pyrazoles.

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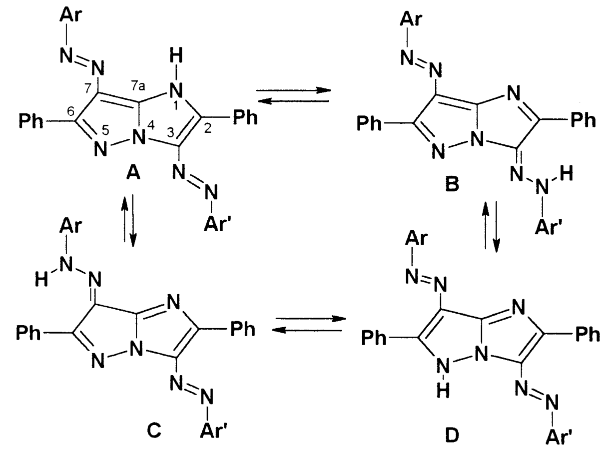

Figure 1.

The structures of the new derivatives **1e**, **f**, **h**, **2e–g** and **3e–h** were evidenced by their microanalyses and spectral (IR, ^{1}H NMR, MS) data.

When equimolar quantities of the hydrazonoyl bromide **1c** and each of the azo derivatives **3a–g** were refluxed in ethanol in the presence of triethylamine, a single product was obtained in each case. Similar reactions of **3c** with each of the hydrazonoyl bromides **1a–h** also yielded one product in each case. On the basis of both microanalyses and spectral data of the isolated products were identified as 3,7-bis(arylazo)-2,6-diphenyl-1*H*-imidazo[1,2-*b*]pyrazoles **4** and **5**, respectively (Scheme 1). The other regioisomeric structures, namely 2,7-bis(arylazo)-3,6-diphenyl-1*H*-imidazo[1,2-*b*]pyrazoles **6** and **7** were discarded on the basis that reaction of 5-amino-3-phenylpyrazole with 2-oxohydrazonoyl halides was reported to afford in all cases examined the respective 3-arylazo-2,6-diaryl-1*H*-imidazo[1,2-*b*]pyrazoles and not the isomeric 2-arylazo-3,6-diaryl-1*H*-imidazo[1,2-*b*]pyrazoles.[14,15]

The IR spectra of the products **4** and **5** revealed in each case a weak NH band near 3200 cm^{-1} (Table 1). Their mass spectra revealed in each case the respective molecular ion peak together with ($M^+ + 1$) and ($M^+ + 2$) peaks. Although such peaks were intense, they were not the base peaks, however. 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 $C_{11}H_6N_3$ ionic fragments. The latter fragment corresponds to either 2-phenyl- or 6-phenyl-1*H*-imidazo[1,2-*b*]pyrazole residue (Table 2). Their NMR spectra in deuterated chloroform exhibited a broad NH proton singlet signal centered at δ 11.5–11.8 (Table 1). The shape of the latter signal did not change with temperature. Although these data are consistent

Table 1. IR and ^{1}H NMR spectral data of compounds **4** and **5**

Compound no.	IR ν (cm^{-1})	^{1}H NMR δ (multiplicity, number of protons)[a]
4a	3120	3.8 (s, 3H), 6.95 (d, 2H), 7.92 (d, 2H), 7.1–7.4 and 8.2–8.47 (m, 15H), 11.8 (s, 1H)
4b	3170	2.4 (s, 3H), 7.24 (d, 2H), 7.37 (d, 2H), 7.4–8.6 (m, 15H), 11.7 (s, 1H)
4c	3150	7.2–8.5 (m, 20H), 11.6 (s, 1H)
4d	3110	8.19 (d, 2H), 8.43 (d, 2H), 7.19–8.14 (m, 15H), 11.5 (s, 1H)
4e	3160	7.4–8.8 (m, 19H), 11.9 (s, 1H)
4f	3155	6.91–8.45 (m, 19H), 11.55 (s, 1H)
4g	3170	7.74 (d, 2H), 7.94 (d, 2H), 7.2–7.4 and 8.1–8.5(m, 15H), 11.7 (s, 1H)
5a	3122	3.8 (s, 3H), 6.95 (d, 2H), 7.92 (d, 2H), 7.1–7.4 and 8.2–8.47 (m, 15H), 11.6 (s, 1H)
5b	3130	2.4 (s, 3H), 7.24 (d, 2H), 7.37 (d, 2H), 7.4–8.6 (m, 15H), 11.6 (s, 1H)
5d	3115	8.19 (d, 2H), 8.43 (d, 2H), 7.19–8.14 (m, 15H), 11.7 (s, 1H)
5e	3130	7.26–8.5 (m, 19H), 11.6 (s, 1H)
5f	3150	7.26–8.5 (m, 19H), 11.55 (s, 1H)
5g	3170	7.52 (d, 2H), 8.33 (d, 2H), 7.6–8.2 and 8.5–8.6 (m, 15H), 11.6 (s, 1H)
5h	3170, 1705	1.7 (t, *J*=7 Hz, 3H), 4.7 (q, *J*=7 Hz, 2H), 7.4–8.7 (m, 19H), 11.66 (s, 1H)

[a] $CDCl_3$.

Table 2. Mass spectral data of the compounds **4** and **5**

Compound no.	*m*/*z* (%)
4a	498 (94), 497 (100), 469 (11), 390 (14), 381 (15), 115 (16), 180 (10), 104 (11), 91 (10), 77 (95)
4b	483 (13), 482 (48), 481 (10), 391 (21), 377 (11), 272 (13), 194 (33), 180 (5), 105 (33), 91 (54), 77 (100)
4c	469 (17), 468 (53), 467 (32), 390 (28), 363 (13), 351 (16), 180 (23), 91 (15), 77 (100)
4d	503 (25), 502 (74), 501 (41), 391 (43), 384 (32), 214 (31), 180 (3), 115 (19), 111 (27), 77 (100)
4e	503 (11), 502 (11), 501 (23), 390 (23), 384 (24), 272 (16), 216 (17), 180 (16), 111 (35), 91 (19), 77 (100)
4f	514 (6), 513 (8), 512 (15), 435 (15), 395 (20), 349 (63), 322 (14), 292 (14), 246 (27), 205 (14), 180 (100), 116 (18), 77 (24)
4g	514 (26), 513 (52), 512 (29), 390 (39), 361 (10), 349 (22), 273 (10), 179 (18), 115 (21), 103 (16), 91 (16), 77 (100)
5a	498 (67), 497 (96), 470 (15), 421 (19), 350 (32), 246 (13), 180 (35), 122 (10), 107 (36), 104 (16), 91 (14), 77 (100)
5b	483 (15), 482 (41), 481 (15), 480 (10), 404 (24), 377 (15), 180 (46), 114 (15), 104 (19), 91 (80), 77 (100)
5d	503 (25), 502 (66), 501 (66), 424 (24), 396 (10), 351 (29), 180 (39), 118 (39), 111 (34), 104 (18), 91 (20), 77 (100)
5e	503 (25), 502 (26), 501 (59), 424 (41), 362 (16), 350 (66), 322 (18), 271 (23), 242 (24), 180 (88), 111 (57), 89 (22),77 (100)
5f	514 (36), 513 (30), 512 (77), 435 (55), 407 (26), 369 (59), 300 (39), 293 (44), 290 (100), 280 (37), 244 (56), 180 (55), 181 (81), 117 (85), 77 (85)
5g	514 (19), 513 (55), 512 (12), 437 (13), 326 (35), 350 (13), 242 (16), 180 (28), 115 (19), 105 (22), 91 (20), 77 (100)
5h	541 (24), 540 (65), 512 (24), 351 (35), 247 (22), 180 (50), 115 (22), 103 (32), 91 (22), 77 (100)

with the assigned structures **4** and **5**, they cannot distinguish between the four possible tautomeric forms **A**–**D** (Fig. 1). They indicate, however, that each of the studied compounds exists predominantly in one tautomeric form and that any other tautomer form, if it were present, it will be at a level of ca. 1% or less so that it would be unlikely detected by any of the spectroscopic methods employed.

To elucidate the actual tautomeric form of compounds **4** and **5**, their electronic absorption spectra and correlations of their acid dissociation constants with the Hammett equation were examined. Their electronic spectra in dioxane revealed in each case two characteristic intense absorption bands in the regions 600–400 and 350–290 nm. The data are summarized in Table 3. Such an absorption pattern is similar to that reported for the azo chromophore.[16] Furthermore, as compounds **4c** and **5c** are the same compound obtained from different precursors, the electronic spectra of **4c**, taken as typical example of the two series investigated, were recorded in solvents of different polarities. The spectra obtained showed little, if any, shift (Table 3). This result indicates that the compounds exist in one tautomeric form, namely the bis(arylazo) form, either **A** or **D** (Fig. 1).

Table 3. Electronic absorption spectra of compounds **4** and **5**

Compound no.	λ_{max} (dioxane) (log ε)
4a	514 (4.33), 289 (4.15)
4b	506 (4.30), 293 (4.14)
4c[a]	502 (4.37), 287 (4.24)
4d	508 (4.30), 289 (4.15)
4e	490 (4.26), 291 (4.14)
4f	495 (4.19), 295 (4.11)
4g	508 (4.55), 323 (4.17)
5a	487 (4.38), 300 (4.28)
5b	510 (4.38), 287 (4.26)
5d	500 (4.39), 288 (4.25)
5e	501 (4.25), 277 (4.15)
5f	503 (4.47), 280 (4.36)
5g	501 (4.37), 324 (4.10)
5h	505 (4.52), 280 (4.48)

[a] Solvent: λ_{max} nm (log ε) ethanol: 514 (4.38), 271 (4.28); chloroform: 494 (4.37), 274 (4.24); acetic acid: 511 (4.33), 288 (4.21); cyclohexane: 494 (4.28), 274 (4.20); pyridine: 498 (4.30), 290 (sh) (4.21); ether: 499 (4.34), 271 (4.28).

Next, the acid dissociation constants (p*K*), of the two series **4a**–**g** and **5a**–**h** were determined by the spectrophotometric method in 80% (v/v) dioxane–water mixture at 27°C and ionic strength of 0.1. From the pH-absorbance data, the p*K* values were calculated (see Section 3) and the results are summarized in Table 4. As shown, the data reveal that the acidity constants of both series **4** and **5** are influenced by the ring substituent, being increased by electron-withdrawing substituents and decreased by electron-donating substituents. Correlation of these p*K* data with Hammett substituent constant σ_x using the least-squares method resulted in the following equations:

$$\mathrm{p}K(\mathbf{4}) = 9.93 - 1.75\sigma_x; \qquad r = 0.995; \; s = \pm 0.03$$

$$\mathrm{p}K(\mathbf{5}) = 9.94 - 1.46\sigma_x; \qquad r = 0.987; \; s = \pm 0.04$$

Table 4. Acid dissociation constants p*K* and p*K** of compounds **4** and **5**

Compound no.	p*K*	λ_{max}[a]	λ_{max}[b]	$\Delta\nu$ (cm^{-1})	p*K**
4a	10.37	467	536	2758	4.63
4b	10.19	465	532	2756	4.48
4c	10.02	460	531	2906	3.98
4d	9.50	460	535	3051	3.15
4e	9.31	455	532	3181	2.68
4f	8.68	454	533	3274	1.74
4g	8.54	500	600	3342	1.59
5a	10.22	465	533	2744	4.51
5b	10.12	462	531	2813	4.27
5d	9.65	458	538	3243	2.91
5e	9.55	458	538	3254	2.78
5f	8.81	458	540	3322	1.90
5g	8.64	498	598	3358	1.66
5h	9.29	470	555	3258	2.50

[a] In acid medium.

[b] In alkaline medium; $s = \pm 0.04$.

where *r* and *s* are the correlation coefficient and standard deviation. Such excellent linear correlations indicate that the compounds studied exist in the 1H-structure, namely the bis(arylazo) form **A** (Fig. 1). This is because if they exist in one of the mixed azo-hydrazone tautomeric forms **B** or **C**, their p*K* values will be better correlated with the enhanced Hammett substituent constant $\sigma-$ rather than σ as the substituent will be in a direct interaction with the negative charge on the nitrogen atom in the conjugate base. The assignment of form **A** is further substantiated by the similarity of the ρ values 1.75 and 1.45 found for the two series studied **4** and **5**, respectively and the similarity of such ρ values with that reported for 2-arylazophenols ($\rho=1.22$).[17] For typical hydrazones, the ρ value was reported to be 2.57.[16] Finally, if the compounds had the 5H-structure, i.e. form **D** (Fig. 1), the ρ value for series **5** will be much less than that of series **4**; i.e. less than 1.0. This is because, in structure **D**, the bridge A′–N=N–C(3)=C(2)–N(1)=C(7a)–C(7)=C(6)– between the acidic site –N(5)H and the substituent in Ar′ group is longer than the bridge Ar–N=N–C(7)=C(6)– between the same acidic site –N(5)H and the substituent in Ar group. Considering the transmissive factors (π' 0.58 and 0.45) of the two extra –N=C– and C=C double bonds, respectively,[21] the value of $\rho(\mathbf{5})$ is expected to be much less than that of $\rho(\mathbf{4})$. This was not found experimentally, however, and therefore the tautomeric form **D** was discarded.

Finally, we examined the correlation of the acidity constants p*K** of **4** and **5** in their corresponding singlet excited states each with the Hammett substituent constant. The values of p*K** were calculated by utilizing the so-called Forster energy-cycle.[18] According to this cycle

$$\mathrm{p}K^* = \mathrm{p}K + 0.625(\Delta\nu)/T$$

where p*K* and p*K** are the acid dissociation constants of the compound under study 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.[19] The results of such calculations are summarized in Table 4. Plots of p*K** for the two series **4** and **5** each vs σ_x were linear. The equations of the regression lines are

$$\mathrm{p}K^*(\mathbf{4}) = 3.90 - 3.04\sigma_x; \qquad r = 0.90; \; s = \pm 0.05$$

$$\mathrm{p}K^*(\mathbf{5}) = 3.84 - 2.70\sigma_x; \qquad r = 0.99; \; s = \pm 0.03$$

As shown, the ρ^* values obtained are larger than those of the ground state. Assuming that the atom connectivity is the same in ground and excited states, such results emphasize the importance of the electronic interactions in the excited state.[19] Furthermore, such linear correlations together with the similarity of the ρ^* values collectively indicate that the studied compounds **4** and **5** exist predominantly in the 1H-structure, namely form **A** (Fig. 1) in their excited states too. This is only to be expected if the lifetime of the excited state before electronic relaxation is too short to allow equilibration with other tautomeric structures.

In conclusion, the results of the present study demonstrate collectively that *N*-aryl 2-oxoethanehydrazonoyl bromides **1** provide useful entry to synthesis of the title bis(arylazo) compounds **4** and **5** and that both series of compounds exist in solution almost exclusively in the 1*H*-bis(arylazo) tautomeric form **A** in both the ground and excited states.

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 chloroform 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.

N-Aryl 2-oxo-2-phenyethanehydrazonoyl bromides **1**,[13] 2-arylhydrazono-3-oxo-3-phenylpropanenitriles **2**[13] and 5-amino-4-arylazo-3-phenylpyrazoles **3**[14] were prepared as previously reported from our laboratory. The physical constants of the new derivatives **1e**, **f**, **h**, **2e–g** and **3e–g** are given below.

3.1.1. *N*-(3-Chlorophenyl) 2-oxo-2-phenylethanehydrazonoyl bromide (1e). Yellow needles, yield 70%, mp 170°C (EtOH), IR ν (KBr) cm^{-1} 3225, 1654; ^{1}H NMR (CDCl$_3$) δ 7.3–8.3 (m, 9H), 8.91 (s, 1H). Anal. calcd (Found) for $C_{14}H_{10}BrClN_2O$ (337.6): C, 49.81 (49.6); H, 2.99 (3.2); N, 8.30 (8.0)%.

3.1.2. *N*-(3-Nitrophenyl) 2-oxo-2-phenylethanehydrazonoyl bromide (1f). Yellow needles, yield 75%, mp 215°C (Dioxane), IR ν (KBr) cm^{-1} 3240, 1653; ^{1}H NMR (CDCl$_3$) δ 7.4–8.2 (m, 9H), 10.5 (s, 1H). Anal. calcd (Found) for $C_{14}H_{10}BrN_3O_3$ (348.2): C, 48.29 (48.5); H, 2.90 (3.2); N, 12.07 (12.3)%.

3.1.3. *N*-(4-Ethoxycarbonylphenyl) 2-oxo-2-phenylethanehydrazonoyl bromide (1h). Yellow needles, yield 80%, mp 180°C (Dioxane), IR ν (KBr) cm^{-1} 3224, 1705, 1654; ^{1}H NMR (CDCl$_3$) δ 1.34 (t, *J*=7 Hz, 3H), 4.31 (q, *J*=7 Hz, 2H), 7.1–8.2 (m, 9H), 9.2 (s, 1H). Anal. calcd (Found) for $C_{17}H_{15}BrN_2O_3$ (375.2): C, 54.42 (54.4); H, 4.03 (4.3); N, 7.47 (7.6)%.

3.1.4. 2-*N*-(3-Chlorphenylhydrazono)-3-oxo-3-phenylpropanenitrile (2e). Yellow needles, yield 90%, mp 188°C (EtOH), IR ν (KBr) cm^{-1} 3220, 2218, 1654; ^{1}H NMR (CDCl$_3$) δ 7.2–8.2 (m, 9H), 9.6 (s, 1H). Anal. calcd (Found) for $C_{15}H_{10}ClN_3O$ (283.7): C, 63.51 (63.6); H, 3.55 (4.0); N, 14.81 (14.5)%.

3.1.5. 2-*N*-(3-Nitrophenylhydrazono)-3-oxo-3-phenylpropanonitrile (2f). Yellow needles, yield 85%, mp 194°C (AcOH), IR ν (KBr) cm^{-1} 3210, 2215, 1635; ^{1}H NMR (CDCl$_3$) δ 7.20–8.10 (m, 9H), 12.0 (s, 1H). Anal. calcd (Found) for $C_{15}H_{10}N_4O_3$ (294.3): C, 61.22 (61.5); H, 3.42 (3.6); N, 19.04 (18.8)%.

3.1.6. 2-*N*-(4-Nitrophenylhydrazono)-3-oxo-3-phenylpropanonitrile (2g). Yellow needles, yield 90%, mp 230°C (AcOH), IR ν (KBr) cm^{-1} 3209, 2214, 1650; ^{1}H NMR (CDCl$_3$) δ 7.26–8.15 (m, 9H), 12.0 (s, 1H). Anal. calcd (Found) for $C_{15}H_{10}N_4O_3$ (294.3): C, 61.22 (61.2); H, 3.42 (3.7); N, 19.04 (18.9)%.

3.1.7. 5-Amino-4-(3-chlorophenylazo)-3-phenylpyrazole (3e). Dark yellow needles, yield 80%, mp 198°C (AcOH), IR ν (KBr) cm^{-1} 3417, 3385; ^{1}H NMR (CDCl$_3$) δ 6.2 (s, 2H), 7.25–8.05 (m, 10H). MS *m/z* (%) 299 (26), 298 (75), 297 (56), 186 (100), 130 (70), 128 (43), 111 (15), 103 (25), 77 (40). Anal. calcd (Found) for $C_{15}H_{12}ClN_5$ (298): C, 60.51 (60.5); H, 4.06 (4.2); N, 23.50 (23.1)%.

3.1.8. 5-Amino-4-(3-nitrophenylazo)-3-phenylpyrazole (3f). Dark yellow needles, yield 75%, mp 210°C (AcOH), IR ν (KBr) cm^{-1} 3418, 3300; ^{1}H NMR (CDCl$_3$) δ 6.7 (s, 2H), 7.42–8.52 (m, 10H). MS *m/z* (%) 309 (19), 308 (100), 186 (96), 130 (65), 128 (41), 103 (30), 77 (29). Anal. calcd (Found) for $C_{15}H_{12}N_6O_2$ (308.3): C, 58.44 (58.5); H, 3.92 (4.2); N, 27.26 (27.0)%.

3.1.9. 5-Amino-4-(4-nitrophenylazo)-3-phenylpyrazole (3g). Dark brown needles, yield 80%, mp 278°C (EtOH), IR ν (KBr) cm^{-1} 3417, 3385; ^{1}H NMR (CDCl$_3$) δ 6.81 (s, 2H), 7.40–8.30 (m, 10H). MS *m/z* (%) 309 (80), 308 (25), 186 (95), 130 (100), 77 (58). Anal. calcd (Found) for $C_{15}H_{12}N_6O_2$ (308.3): C, 58.44 (58.4); H, 3.92 (4.0); N, 27.26 (27.1)%.

3.1.10. 3,7-Bis(arylazo)-2,6-diphenyl-1*H*-imidazo[1,2-*b*]pyrazoles (4 and 5). *General procedure*. To a mixture of hydrazonoyl bromide **1c** and the appropriate pyrazole derivative **3** (5 mmol each) in dioxane (30 mL) was added triethylamine (0.7 mL, 5 mmol). The reaction mixture was refluxed for 3 h, cooled and poured onto cold water while stirring. The solid that precipitated was filtered off, dried and crystallized from dioxane or acetic acid to give the respective **4**.

Repetition of the same procedure using the pyrazole derivative **3c** with the hydrazonoyl bromides **1a–h** yielded the respective **5a–h**, respectively.

Table 5. Physical constants of 2,6-diphenyl-3,7-bis(arylazo)-1*H*-imidazo-[1,2-*b*]pyrazoles **4**

Compound no.	Yield (%)	Mp (°C) (solvent)[a]	Molecular formula	Anal. calcd/found (%)		
				C	H	N
4a	80	230 (a) dark brown needles	$C_{30}H_{23}N_7O$ (497.5)	72.42 72.6	4.66 4.6	19.70 19.5
4b	85	262 (a) dark green needles	$C_{30}H_{23}N_7$ (481.6)	74.83 74.6	4.81 4.8	20.36 20.1
4c	90	265 (a) dark green needles	$C_{29}H_{21}N_7$ (467.5)	74.50 74.5	4.53 4.8	20.97 21.0
4d	90	260 (a) dark red plates	$C_{29}H_{20}ClN_7$ (501.9)	69.39 69.2	4.01 4.4	19.53 19.5
4e	85	268 (a) dark green needles	$C_{29}H_{20}ClN_7$ (501.9)	69.39 69.2	4.01 4.1	19.53 19.5
4f	85	254 (a) dark red needles	$C_{29}H_{20}N_8O_2$ (512.5)	67.96 67.8	3.93 4.0	21.86 21.8
4g	90	261 (b) dark brown plates	$C_{29}H_{20}N_8O_2$ (512.5)	67.96 67.9	3.93 4.1	21.86 21.7

[a] Solvent of crystallization: (a) acetic acid; (b) dioxane.

Table 6. Physical constants of 2,6-diphenyl-3,7-bis(arylazo)-1*H*-imidazo-[1,2-*b*]pyrazoles **5**

Compound no.	Yield (%)	Mp (°C) (solvent)[a]	Molecular formula	Anal. calcd/found (%)		
				C	H	N
5a	85	230 (a) dark brown needles	$C_{30}H_{23}N_7O$ (497.5)	72.42 72.6	4.66 4.7	19.70 19.8
5b	70	256 (a) dark green needles	$C_{30}H_{23}N_7$ (481.6)	74.83 74.8	4.81 5.0	20.36 20.2
5d	90	254 (a) dark brown needles	$C_{29}H_{20}ClN_7$ (501.9)	69.39 69.1	4.01 4.1	19.53 19.5
5e	75	184 (a) dark red needles	$C_{29}H_{20}ClN_7$ (501.9)	69.39 69.2	4.01 4.0	19.53 19.4
5f	70	195 (a) dark red needles	$C_{29}H_{20}N_8O_2$ (512.5)	67.96 67.6	3.93 4.1	21.86 22.2
5g	90	252 (b) dark brown needles	$C_{29}H_{20}N_8O_2$ (512.5)	67.96 67.7	3.93 4.1	21.86 21.7
5h	70	222 (a) dark red needles	$C_{32}H_{25}N_7O_2$ (539.6)	71.23 70.9	4.67 4.5	18.17 18.1

[a] Solvent of crystallization: (a) acetic acid; (b) dioxane.

The physical constants of the products **4a–g** and **5a–h** isolated are given in Tables 5 and 6, respectively.

3.2. p*K* 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 0.01. An Orion 420A 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 Haas[20] 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.[21] The p*K* values were reproducible to ±0.02 p*K* unit. The results are given in Table 4.

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