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Synthesis and tautomeric structure of 7-arylhydrazono-3,5-diphenyl-5*H*-pyrazolo[5,1-*c*][1,2,4]triazol-6(7*H*)-ones in its ground and excited states

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Abstract

A series of 7-arylhydrazono-3,5-diphenyl-5*H*-pyrazolo[5,1-*c*][1,2,4]triazol-6(7*H*)-ones **4a-j** were synthesized from the reactions of 4-phenylamino-5-phenyl-4*H*-1,2,4-triazole-3-thiol **1** and ethyl arylhydrazonochloro acetate **2** and their acid dissociation constant pK_a and pK_a^*, in the ground and excited states, respectively, were determined. Both pK_a and pK_a^* constants were correlated with the Hammett equation. The results of such correlations together with the spectroscopic data indicated that the studied compounds exist predominantly in the hydrazone tautomeric form in both ground and excited states.

1. Introduction

In continuation of our previous studies on the synthesis and elucidation of the tautomeric structures of arylazo heterocycles [1-6], Our interest in arylazo heterocycles is due to the fact that many of such dyes have many industrial applications in the fields of hair dyeing, disperse dyes, ink-jet inks, laser printing and laser materials [7-13]. On the other hand, pyrazolo[5,1-*c*][1,2,4]triazol derivatives are extensively used in modern photographic color material such as magenta coupler in photosensitive emulsion layer [14,15]. In view of these findings, we wish to report herein the synthesis of a series of the title compounds **4** *via* reactions of hydrazonoyl halides **2** with 4-phenylamino-5-phenyl-4*H*-1,2,4-triazole-3-thiol **1** and determine their tautomeric structure prior to exploring their applications. This is because the target arylazo compounds can have one or more of four possible tautomeric forms (Chart 1).

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2. 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 spectrophotometers. ^{1}H-NMR spectra were recorded in deuterated dimethyl sulfoxide using a Varian Gemini 300 NMR spectrometer. Mass spectra were recorded on a GCMS-QP1000 EX Shimadzu and GCMS 5988-A HP spectrometers. Electronic absorption spectra were recorded on Perkin- Elmer Lambada 40 spectrophotometer. Elemental analyses were carried using German made Elementar Vario LIII CHNS analyzer at the Microanalytical Laboratory of Cairo University, Giza, Egypt. Solvents were generally distilled and dried by standard literature procedure prior to use. The 4-phenylamino-5-phenyl-4*H*-1,2,4-triazole-3-thiol **1** [16] and The Hydrazonoyl halides **2a-i** [17] were prepared by literature methods.

*2.1. Ethyl-[(4-phenylamino-5-phenyl-4H-1,2,4-triazol-3-yl)thio][Arylhydrazono]acetate (**3a-f**)*

To a solution of 4-phenylamino-5-phenyl-4*H*-1,2,4-triazole-3-thiol **1** and ethyl phenylhydrazonochloroacetate **2a-f** (5 mmol each) in absolute ethanol (40 mL) was added triethylamine (0.7 mL, 5 mmol). The reaction mixture was stirred for 2 h at room temperature, and then diluted with water. The solid that precipitated was filtered off, dried and finally crystallized from the appropriate solvent to give the respective thiohydrazonate ester **3a-f**. The compounds **3a-f** prepared, together with their physical constants, are listed subsequently.

*2.1.1. Ethyl-[(4-phenylamino-5-phenyl-4H-1,2,4-triazol-3-yl)thio][(4-methoxyphenyl)hydrazono] acetate (**3a**)*

Yellow solid (1.51 g, 62%); m.p = 195 ^{o}C (EtOH); IR (KBr) ν_{max} (cm^{-1}): 3360, 3305 (2NH), 1710 (CO), 1650 (C=N); ^{1}H NMR (DMSO-d_6) (δppm): 1.36 (t, 3H, CH_3), 3.55 (s, 3H, CH_3), 4.49 (q, 2H, CH_2), 7.12-7.94 (m, 14H, ArH), 10.95 (s, 2H, 2NH); MS m/z (%) 488 (M^+, 15), 457 (25), 344 (20), 271 (19), 150 (35), 105 (100), 91 (57), 75 (80). Anal. Calcd. for $C_{25}H_{24}N_6O_3S$ (488.57): C, 61.46; H, 4.95; N, 17.20; S, 6.56. Found: C, 61.41; H, 4.85; N, 17.10; S, 6.48 %.

*2.1.2. Ethyl-[(4-phenylamino-5-phenyl-4H-1,2,4-triazol-3-yl)thio][(4-methylphenyl)hydrazono]-acetate (**3b**)*

Yellow solid (1.41 g, 60%), m.p. 205 ^{o}C (EtOH); IR (KBr) ν_{max} (cm^{-1}): 3360, 3300 (2NH), 1711 (CO), 1640 (C=N); ^{1}H NMR (DMSO-d_6) (δppm): 1.26 (t, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.30 (q, 2H, CH_2), 7.25-7.81(m, 14H, ArH), 11.25 (s, 2H, 2NH); MS m/z (%) 472 (M^+, 4.5), 470 (4.5), 382 (44), 276 (10), 150 (14), 105 (100), 91 (26), 77 (60); Anal. Calcd. For $C_{25}H_{24}N_6O_2S$ (472.57): C, 63.54; H, 5.12; N, 17.78; S, 6.78. Found: C, 63.5; H, 5.11; N, 17.72; S, 6.70 %.

*2.1.3. Ethyl-[(4-phenylamino-5-phenyl-4H-1,2,4-triazol-3-yl)thio][(3-methylphenyl)hydrazono]-acetate (**3c**)*

Yellow solid (1.51g, 64%), m.p. 200 ^{o}C (EtOH); IR (KBr) ν_{max} (cm^{-1}): 3355, 3290 (2NH), 1718 (CO), 1638 (C=N); ^{1}H NMR (DMSO-d_6) (δppm): 1.30 (t, 3H, CH_3), 2.31 (s, 3H, CH_3), 4.34 (q, 2H, CH_2), 7.20-7.78(m, 14H, ArH), 11.19 (s, 2H, 2NH); MS m/z (%)

472 (M^+, 3.5), 470 (5.5), 382 (40), 276 (15), 150 (17), 105 (100), 91 (36), 77 (69); Anal. Calcd. For $C_{25}H_{24}N_6O_2S$ (472.57): C, 63.54; H, 5.12; N, 17.78; S, 6.78. Found: C, 63.48; H, 5.01; N, 17.65; S, 6.81 %.

*2.1.4 Ethyl-[(4-phenylamino-5-phenyl-4H-1,2,4-triazol-3-yl)thio](phenylhydrazono)acetate (**3d**)*

Pale yellow solid (1.60g, 70 %); m.p = 182 ^oC (EtOH/DMF); IR (KBr) ν_{max} (cm^{-1}): 3340, 3275 (2NH), 1714 (CO), 1645 (C=N); ^1H NMR (DMSO-d_6) (δppm): 1.23 (t, 3H, CH_3), 4.28 (q, 2H, CH_2), 7.29-7.91 (m, 15H, ArH), 10.21 (s, H, NH); 11.23 (s, H, NH); MS, m/z (%) 458 (M^+, 31), 428 (57), 411(52), 151 (24), 105 (100), 91 (33), 76 (68); Anal. Calcd. For $C_{24}H_{22}N_6O_2S$ (458.55): C, 62.87; H, 4.84; N, 18.33; S, 6.99. Found: C, 62.81; H, 4.82; N, 18.30; S, 6.89%.

*2.1.5. Ethyl-[(4-phenylamino-5-phenyl-4H-1,2,4-triazol-3-yl)-thio][(4-chlorophenyl) hydrazono]-acetate (**3e**)*

Yellow solid (1.67g, 68%); m.p = 210 ^oC (EtOH); IR (KBr) ν_{max} (cm^{-1}): 3340, 3270 (2NH), 1724 (CO), 1645 (C=N); ^1H NMR (DMSO-d_6) (δppm): 1.37 (t, 3H, CH_3), 4.40 (q, 2H, CH_2), 7.30-7.84 (m, 14H, ArH), 11.25 (s, 2H, 2NH); MS m/z (%) 494 (M^++2, 7), 492 (M^+, 20), 384 (23), 275 (15), 150 (21), 105 (100), 91 (33), 75 (63). Anal. Calcd. For $C_{24}H_{21}ClN_6O_2S$ (492.99): C, 58.47; H, 4.29; Cl, 7.19; N, 17.05; S, 6.50. Found: C, 58.38; H, 4.21; Cl, 7.10; N, 17.00; S, 6.44 %.

*2.1.6 Ethyl-[(4-phenylamino-5-phenyl-4H-1,2,4-triazol-3-yl-)thio][(3-chlorophenyl) hydrazono]-acetate (**3f**)*

Yellow solid (1.60g, 65%); m.p = 185 ^oC (EtOH); IR (KBr) ν_{max} (cm^{-1}): 3340, 3270 (2NH), 1720 (CO), 1635 (C=N); ^1H NMR (DMSO-d_6) (δppm): 1.32 (t, 3H, CH_3), 4.46 (q, 2H, CH_2), 7.20-7.74 (m, 14H, ArH), 11.35 (s, 2H, 2NH); MS m/z (%) 494 (M^++2, 5), 492 (M^+, 13), 384 (20), 275 (10), 150 (28), 105 (100), 91 (43), 75 (68). Anal. Calcd. For $C_{24}H_{21}ClN_6O_2S$ (492.99): C, 58.47; H, 4.29; Cl, 7.19; N, 17.05; S, 6.50. Found: C, 58.34; H, 4.19; Cl, 7.12; N, 16.98; S, 6.47 %.

2.2. 3,5-diphenyl-7- Arylhydrazono-5H-pyrazolo[5,1-c][1,2,4] triazolo-6(7H)-one(4)

Method A

To a solution of the appropriate thiohydrazonate **3a-f** (5 mmol) in absolute ethanol (40 mL) was added triethylamine (0.7 mL, 5 mmol). The reaction mixture was refluxed for 5 h, cooled and poured onto cold water. The solid that precipitated was filtered off, dried and crystallized from the appropriate solvent to give the respective **4a-f**.

Method B

To a solution of 4-phenylamino-5-phenyl-4*H*-1,2,4-triazole-3-thiol **1** and ethyl arylhydrazono-chloroacetate **2a-i** (5 mmol each) in absolute ethanol (40 mL) was added triethylamine (0.7 mL, 5 mmol). The reaction mixture was refluxed for 10 h, cooled and poured onto cold water. The solid that precipitated was filtered off, dried and crystallized from the appropriate solvent to give the respective **4a-i**.

*2.2.1. 3,5-diphenyl-7-(4-methoxyphenylhydrazono)-5H-pyrazolo [5,1-c][1,2,4]triazolo-6(7H)one (**4a**)*

Yellow solid (1.33 g, 65%), m.p. 275-276 °C (EtOH/DMF); IR (KBr) ν_{max} (cm^{-1}): 3150 (NH), 1708 (CO); ^{1}H NMR (DMSO-d_6) (δppm): 3.72 (s, 3H, CH_3), 7.10-7.81(m, 14H, ArH), 10.11 (s, 1H, NH); MS, m/z (%) 410(M^+, 45), 341(75), 290(32), 155(100), 91(42); Anal. Calcd. For $C_{23}H_{18}N_6O_2$ (410.44): C, 67.31; H, 4.42; N, 20.48. Found: C, 67.28; H, 4.37; N, 20.38 %.

*2.2.2. 3,5-diphenyl-7-(4-methylphenylhydrazono)-5H-pyrazolo [5,1-c][1,2,4]triazolo-6(7H)-one (**4b**)*

Pale yellow solid (1.58 g, 80%), m.p. 255-256 °C (EtOH/DMF); IR (KBr) ν_{max} (cm^{-1}): 3190(NH), 1710(CO); ^{1}H NMR (DMSO-d_6) (νppm): 2.35(s, 3H, CH_3), 7.19-7.91(m, 14H, ArH), 10.21(s, 1H, NH),; MS, m/z (%) 394(M^+, 35), 326(81), 280(21), 155(100), 91(32); Anal. Calcd. For $C_{23}H_{18}N_6O$ (394.44): C, 70.04; H, 4.60; N, 21.31. Found: C, 69.85; H, 4.54; N, 21.29 %.

*2.2.3. 3,5-diphenyl-7-(3-methylphenylhydrazono)-5H-pyrazolo [5,1-c][1,2,4]triazolo-6(7H)-one (**4c**)*

Pale yellow solid (1.47ν, 75%), m.p. 245-246 °C (EtOH/DMF); IR (KBr) n_{max} (cm^{-1}): 3170 (NH), 1718(CO); ^{1}H NMR (DMSO-d_6) (δppm): 2.14 (s, 3H, CH_3), 7.72-8.41(m, 14H, ArH), 10.59(s, 1H, NH),; MS, m/z (%) 394(M^+, 23), 326(74), 280(20), 155(100), 91(38); Anal. Calcd. For $C_{23}H_{18}N_6O$ (394.44): C, 70.04; H, 4.60; N, 21.31. Found: C, 69.98; H, 4.58; N, 21.28%

*2.2.4. 3,5-diphenyl-7-(phenylhydrazono)-5H-pyrazolo[5,1-c][1,2,4]triazolo-6-(7H)-one (**4d**)*

Pale yellow solid (1.43 g, 75%), m.p. 285-287 °C (EtOH/DMF); IR (KBr) ν_{max} (cm^{-1}) 3120 (NH), 1698 (CO); ^{1}H NMR (DMSO-d_6) (δppm): 6.92-8.40 (m, 15H, ArH), 10.59 (s, 1H, NH); MS, m/z (%) 380 (M^+, 100), 310(22), 261(23), 155(48), 77(36); Anal. Calcd. For $C_{22}H_{16}N_6O$ (380.41): C, 69.46; H, 4.24; N, 22.09. Found: C, 69.41; H, 4.20; N, 22.00 %.

*2.2.5. 3,5-diphenyl-7-(4-chlorophenylhydrazono)-5H-pyrazolo [5,1-c][1,2,4]triazolo-6(7H)-one (**4e**)*

Yellow solid (1.56 g, 75%), m.p. 305 °C (DMF); IR (KBr) ν_{max} (cm^{-1}): 3150(NH), 1700 (CO); ^{1}H NMR (DMSO-d_6) (δppm): 7.15-7.99 (m, 14H, ArH), 10.35 (s, 1H, NH); MS, m/z (%) 416 (M^++2, 25), 414(M^+, 77), 345(55), 155(100), 77(16); Anal. Calcd. For $C_{22}H_{15}ClN_6O$ (414.86): C, 63.70; H, 3.64; Cl, 8.55; N, 20.26. Found: C, 63.68; H, 3.52; Cl, 8.42; N, 20.15 %.

*2.2.6. 3,5-diphenyl-7-(3-chlorophenylhydrazono)-5H-pyrazolo [5,1-c][1,2,4]triazolo-6(7H)-one (**4f**)*

Yellow solid (1.45 g, 70%), m.p. 292 °C (DMF); IR (KBr) ν_{max} (cm^{-1}) 3100(NH), 1708 (CO); ^{1}H NMR (DMSO-d_6) (δppm): 7.95-8.43 (m, 14H, ArH), 10.70 (s, 1H, NH); MS, m/z (%) 416 (M^++2, 15), 414(M^+, 44), 345(52), 155(100), 77(26); Anal. Calcd. For $C_{22}H_{15}ClN_6O$ (414.86): C, 63.70; H, 3.64; Cl, 8.55; N, 20.26. Found: C, 63.65; H, 3.60; Cl, 8.50; N, 20.11 %.

*2.2.7. 3,5-diphenyl-7-(3-nitrophenylhydrazono)-5H-pyrazolo [5,1-c][1,2,4]triazolo-6(7H)-one(**4g**)*

Yellow solid (1.38 g, 65%), m.p. 301 °C (DMF); IR (KBr) ν_{max} (cm^{-1}) 3110 (NH), 1715 (CO); ^{1}H NMR (DMSO-d_6) (δppm): 7.47-8.44(m, 14H, ArH), 10.55 (s, 1H, NH); MS, m/z (%) 426 (M^++1, 42), 425(M^+, 31), 297(55), 178(74), 161(55), 155(100); Anal. Calcd. For $C_{22}H_{15}N_7O_3$ (425.41): C, 62.12; H, 3.55; N, 23.05. Found: C, 62.01; H, 3.49; N, 22.96 %.

2.2.8. 3,5-diphenyl-7-(4-nitrophenylhydrazono)-5H-pyrazolo [5,1-c][1,2,4]triazolo-6(7H)-one ***(4h)***

Orange solid (1.59 g, 75%), m.p. 310 ^{o}C (DMF); IR (KBr) ν_{max} (cm^{-1}) 3147 (NH),1704 (CO); ^{1}H NMR (DMSO-d_6) (δppm): 7.07-8.35(m, 14H, ArH), 10.95 (s, 1H, NH); MS, m/z (%) 426 (M^{+}+1, 40), 425(M^{+}, 21), 297(60), 178(83), 161(58), 155(100); Anal. Calcd. For $C_{22}H_{15}N_7O_3$ (425.41): C, 62.12; H, 3.55; N, 23.05. Found: C, 62.11; H, 3.54; N, 23 %.

2.2.9. 3,5-diphenyl-7-(4-Acetylphenylhydrazono)-5H-pyrazolo [5,1-c][1,2,4]triazolo-6(7H)-one ***(4i)***

Orange solid (1.64 g, 78%), m.p. 305 ^{o}C (Dioxane); IR (KBr) ν_{max} (cm^{-1}) 3159 (NH), 1689 (CO), 1706 (CO); ^{1}H NMR (DMSO-d_6) (δppm): 2.30 (s, 3H, CH_3), 7.05-8.53 (m, 14H, ArH), 10.71 (s, 1H, NH); MS, m/z (%) 423 (M^{+}+1, 10), 422(M^{+}, 32), 297(55), 178(73), 161(62), 155(100); Anal. Calcd. For $C_{24}H_{18}N_6O_2$ (422.45): C, 68.24; H, 4.29; N, 19.89. Found: C, 68.18; H, 4.18; N, 19.68 %

2.3. pKa Determination of compounds ***4a-i***

The acid dissociation constants pKa values of the compounds 4 were determined spectrophotometrically in 80% (v/v) dioxane/water mixture at 27 0C 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 [5] namely:

$$-\log [H] = B + \log UH$$

Where log UH 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 0C. The value of log UH was found to be -0.48. The experimental procedure followed in the determination of pKa constants and their calculations from the absorbance-pH data are as previously described [2].The pKa values were reproducible to -0.02 pKa unit. The results are given in Tables 2–4.

3. Results and discussion

Refluxing equimolar quantities of each of the of 4-phenylamino-5-phenyl-4*H*-1,2,4-triazole-3-thiol **1** and each of the ethyl arylhydrazonochloroacetate **2a-i** in ethanol in the presence of triethylamine gave, in each case, one product as evidenced by tlc analysis. The corresponding [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine intermediates which were non-isolable under the reaction conditions and so underwent *in situ* thermal desulfurization [18,19] and ring contraction to afford the corresponding 7-arylhydrazono-3,5-diphenyl-5*H*-pyrazolo[5,1-*c*][1,2,4]triazol-6(7*H*)-one **4a-i** as the solid products. To account for the formation of **4** is depicted in (Scheme 1). The involvement of the thiohydrazonate esters **3** as intermediates in the proposed mechanism was evidenced by alternate synthesis of **4**. Thus, reaction of 4-phenylamino-5-phenyl-4*H*-1,2,4-triazole-3-thiol **1** with ethyl arylhydrazonochloroacetate **2a-f** in ethanol in the presence of triethylamine at room temperature yielded the respective thiohydrazonate esters **3a-f** [2]. The isolable product

3a-f was refluxed in ethanol in the presence of triethylamine gave the products **4a-f** that proved identical in all respects (mp, mixed mp., IR, UV) with those obtained above from refluxing of **1** and ethyl arylhydrazonochloroacetate **2a-i** (Scheme 1).

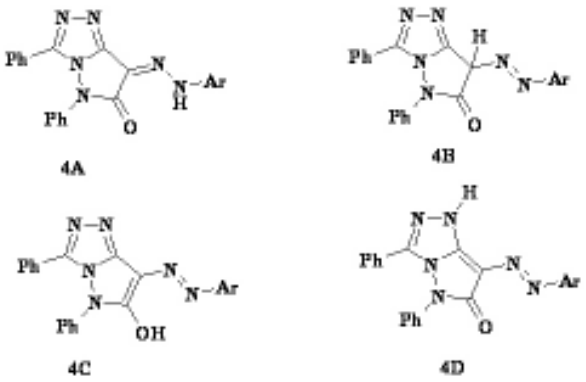
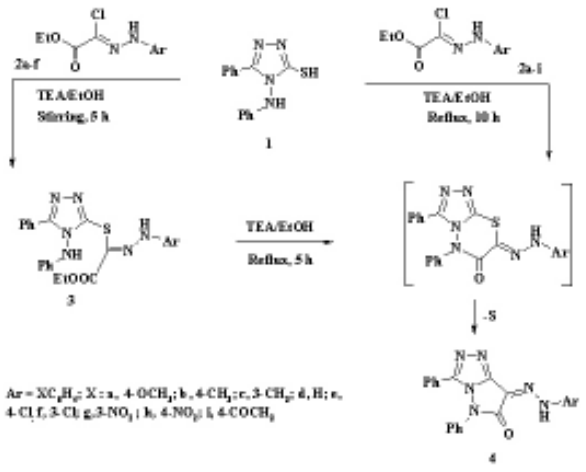


Chart 1. The possible tautomeric forms of 7-arylhydrazono-3,5-diphenyl-5*H*-pyrazolo[5,1-*c*][1,2,4]triazol-6(7*H*)-ones (**4**)



Scheme 1. 7-arylhydrazono-3,5-diphenyl-5*H*-pyrazolo[5,1-*c*][1,2,4]triazol-6(7*H*)-ones

The mass spectra of the latter products **4** revealed the molecular ion peaks at the expected m/z values and their elemental analysis data were consistent with their assigned structures. Their IR spectra showed, in each case, one carbonyl band near 1700 cm^{-1} and one NH band in the region 3190-3100 cm^{-1}. the observed wave number of the CO stretching band in compounds **4** seems to result from the possible strong chlation with the hydrazone NH and conjugation with the C=N double bond as required by the hydrazone form **4A** [20] (Chart 1). These data seem to be consistent with tautomeric form **4A** for the compounds prepared (Chart 1).

The electronic absorption spectra data of the studied compounds **4a-i** are summarized in (Table 1). As shown, each of the compounds **4** in dioxane exhibits two characteristic absorption bands in

Table 1
Electronic absorption spectra of the compounds **4a-i** in ethanol

Compd. no.	λ_{max} (log ε)	Compd. no.	λ_{max} (log ε)
4a	392 (3.78), 305 (4.12)	**4f**	390 (4.34), 306 (4.49)
4b	386 (3.85), 300 (4.22)	**4g**	395 (4.50), 310 (4.45)
4c	385 (4.21), 295(4.05)	**4h**	405(4.56), 312(4.34)
4d[a]	380 (4.10), 308 (4.40)	**4i**	395 (4.42), 315 (4.26)
4e	374 (4.04), 298 (4.20)		

[a]solvent: λmax (nm) (Log ε) Ethanol: 380 (4.10), 308 (4.40); Chloroform: 388 (4.14), 312 (4.11); Acetic acid: 392 (4.25), 312 (4.28); Cyclohexane: 404 (4.27), 305 (4.42); Pyridine: 409 (4.10); 325 (4.10); Ether: 397 (4.03),310 (sh.).

Table 2
Acid dissociation constants pK and pK* of compounds **4a-i**

Compd. No.	σ	σ	pK	λ_{max} (a)	λ_{max} (b)	$\Delta\nu cm^{-1}$	pK*
4a	-0.27	-0.27	10.55	378	452	4331	1.88
4b	-0.17	-0.17	10.21	384	462	4396	1.41
4c	-0.07	-0.07	9.98	382	460	4439	1.10
4d	0	0	9.78	390	473	4499	0.78
4e	0.23	0.23	9.4	394	482	4634	0.13
4f	0.37	0.37	9.12	400	493	4716	-0.31
4g	0.71	0.71	8.46	400	498	4919	-1.38
4h	0.78	1.28	7.35	410	525	5342	-3.33
4i	0.5	0.64	8.71	401	500	5057	-1.16

(a) in acid medium, (b) in alkaline medium

the regions 374-405 and 295-315 nm. Such absorption pattern is similar to that of typical hydrazone chromophore [6, 21]. Furthermore, the spectra of **4d**, taken as a typical example of the series studied, in solvents of different polarities showed little, if any, shift (Table 1). This finding while it suggests that compounds **4** exist in one tautomeric form, it excludes the azo tautomeric forms **4B-D** (Chart 1).

To provide further evidence for the tautomeric form **4A** assigned to the products **4**, the acid dissociation constants, pKa of the series prepared were determined and their correlation by the Hammett equation was tested [22,23]. The pKa values for the series **4a-i** were determined spectrophotometrically at 27 °C in 80% dioxane–water mixture (v/v). In all determinations the ionic strength μ was kept constant at 0.1. From the pH-absorbance data. Typical absorption spectra of **4d** in such buffer solutions are shown in (Figs. 1 and 2). The value of pKa was calculated (See experimental).

The pKa values determined for the compounds **4a-i** are listed in (Table 2). The pKa values were

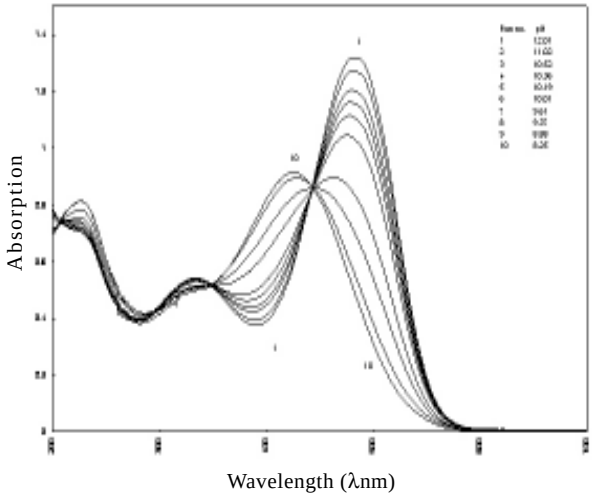


Fig. 1. Electronic absorption spectra of (4d), in solution of different pH values (20% dioxane-water) at 27^{0}C and μ=0.10

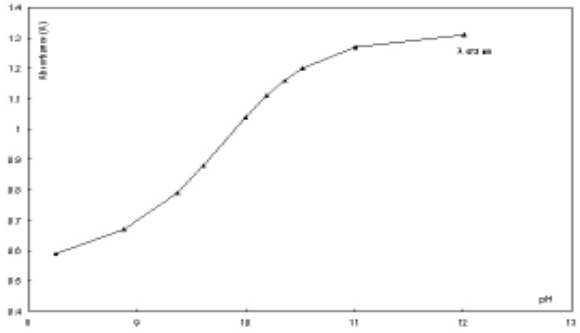


Fig. 2 Spectrphotometric titration curve of (**4d**), at λ max.473 nm in 20% dioxane -water at 27^{0}C and μ=0.10

plotted *versus* the Hammett substituent constants sx and s$^-$x as shown in (Fig. 3 and 4) [24].

The equations corresponding to the straight lines obtained are:

pKa = 9.860 – 2.51 σ_X; r^2 = 0.935; s = ± 0.104
pKa = 9.876 – 1.977 σ_X^-; r^2 = 0.994; s = ± 0.041

where r is the correlation coefficient and s is the standard deviation. From these values of r and s, the pKa data from **4a-i** seem to be better correlated with the enhanced Hammett substituent constant σ^-_x. This finding indicates that compounds **4a-i** exist in the hydrazone form **4A** in solution. This is because if **4** exist as equilibrium mixture of **4A-D** (Scheme 1 and Chart 1) no linear relations between pK and σ^-_x will be observed. Furthermore, the value of the reaction constant ρ = 1.977 seems to be in favor of the hydrazone form **4A** as it is in good agreement with those reported for similar hydrazones and not arylazo derivatives [25,26]. If the azo form **4C-D** were the predominant tautomers for the studied compounds **4**, the value of the reaction constant ρ would have been not more than 0.75.

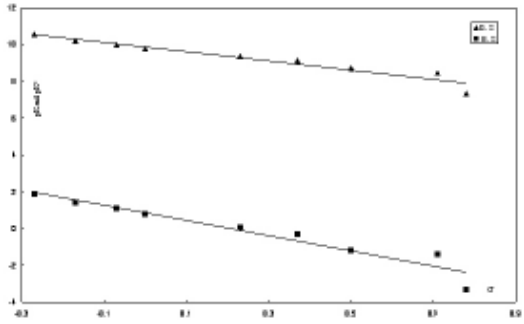


Fig. 3 Correlation of pKa and pKa* of 7-arylhydrazono-3,5-diphenyl-5*H*-pyrazolo[5,1-*c*][1,2,4]triazol-6(7*H*)-ones (4a-i) with Hammett substituent constant, σ_X

This is because the transmissive factor for the bridge –C=C-N=N- in the azo form 4C-D is expected to be 0.32 as the transmissive factors of the –C=C- and –N=N- bridges were reported to be 0.47 and 0.69, respectively [27, 28].

Next, the acid dissociation constants pK*'s of the studied compounds in excited state were

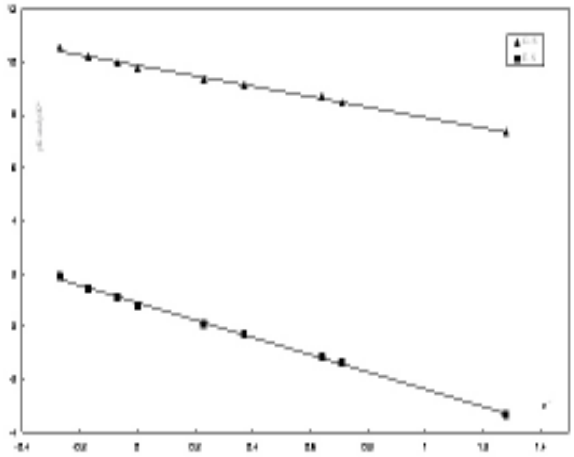


Fig. 4 Correlation of pKa and pKa* of 7-arylhydrazono-3,5-diphenyl-5*H*-pyrazolo[5,1-*c*][1,2,4]triazol-6(7*H*)-ones (4a-i) with Hammett substituent constant, σ_X^-

calculated by utilizing the Forester energy cycle [28-30]. According to this cycle

$$pK^* = pK + 0.625\ (\Delta\nu)/T$$

where pK and pK* are the acid dissociation constants in the ground and excited states, respectively and $\Delta\nu$ represents the frequency difference in cm^{-1} between the values of the absorption maximum λmax of the compound in acid and alkaline media. The results of such calculations are summarized in (Table 2). Correlation of these data of pK* with σx and $\sigma^- x$ are shown in (Fig. 3 and 4), respectively. The linear equations corresponding to such correlations are:

$$pK^* = 0.853 - 4.137\sigma_X,\ r^2 = 0.925,\ s = \pm 0.112$$

$$pK^* = 0.887 - 3.276\ \sigma_X^-,\ r^2 = 0.998,\ s = \pm 0.021$$

Such linear equations indicate that studied compounds **4a-i** are predominantly in the hydrazone tautomeric form in their excited states. The larger value of ρ* emphasizes the importance of the electronic interaction in the excited state [4].

In conclusion, From the foregoing results, we can indicate that hydrazonoyl halides are useful precursors for synthesis of the title arylhydrazono 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 hydrazone tautomeric form **4A** in both ground and excited states.

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