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Pyrazole과 Pyrazolotriazole 유도체의 합성 및 특성 연구

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Synthesis, Fastness and Spectral Properties of Some New Azo Pyrazole and Pyrazolotriazole Derivatives

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요약. 5-Amino-1,3-diaryl-pyrazoles **1a-c** 와 다양한 aryl amine의diazonium salts를 반응시켜서 1,3-diaryl-5-amino-4-arylazo-pyrazoles **3a-l**을 합성하였으며, 몇 가지 화합물은 5-amino-1,3-diaryl-4-nitroso-1*H*-pyrazoles **2a-c**와 aryl amine의 diazonium salts를 반응시켜서 얻었다. 합성한 azo 유도체 화합물 **3a-l**을 DMF 용매 속에서 cupric acetate와 산화반응시켜서 2,4,6-triaryl-2,4-dihydropyrazolo [4,3-*d*]-1,2,3-triazoles **4a-l**을 합성하였으며, 합성한 cyclic triazoles에 대한 형광 특성을 측정하였다. 한편, Diazotization of sodium nitrite/ortho-phosphoric acid 조건에서 5-amino-1,3-diaryl-1*H*-pyrazoles **1a-c**를 diazotization화 반응시킨 다음에, aryl amines과 반응시켜서 *o*-aminoazo compounds **5a-f**를 합성하였다. 합성한 화합물 **5a-f**를 pyridine/cupric acetate 반응 조건에서 반응시켜서 triazole **6a-f**들을 합성하였으며, 얻어진 화합물 **6a-f**을 aryl diazonium salts과 반응시켜서 화합물 **7a-j**을 합성하였다. 합성한 염료 화합물을 polyesters에 분산염료와 정착성을 측정하였다.

주제어: Pyrazolo[4,3-*d*]-1,2,3-triazoles, *o*-Aminoazo 화합물, 형광 특성, 정착성

ABSTRACT. Coupling of 5-amino-1,3-diaryl-pyrazoles **1a-c** with diazonium salts of different aryl amines gave a series of novel 1,3-diaryl-5-amino-4-arylazopyrazoles **3a-l**. Such compounds could be also obtained by reaction of 5-amino-1,3-diaryl-4-nitroso-1*H*-pyrazoles **2a-c** with different aryl amines in alkaline medium. Oxidation of azo derivatives **3a-l** with cupric acetate, in dimethyl formamide and stream of air, gave 2,4,6-triaryl-2,4-dihydropyrazolo [4,3-*d*]-1,2,3-triazoles **4a-l**. and the fluorescence properties of the cyclic triazoles were studied. Diazotization of 5-amino-1,3-diaryl-1*H*-pyrazoles **1a-c** by sodium nitrite in ortho-phosphoric acid followed by coupling with some aryl amines gave *o*-aminoazo compounds **5a-f**. Cyclisation of compounds **5a-f** in pyridine and cupric acetate gave the corresponding triazoles **6a-f**. The coupling of compounds **6a-f** with different aryl diazonium salts gave compounds **7a-j**. The synthesized dyes were applied to polyesters as disperse dyes and the fastness properties were evaluated.

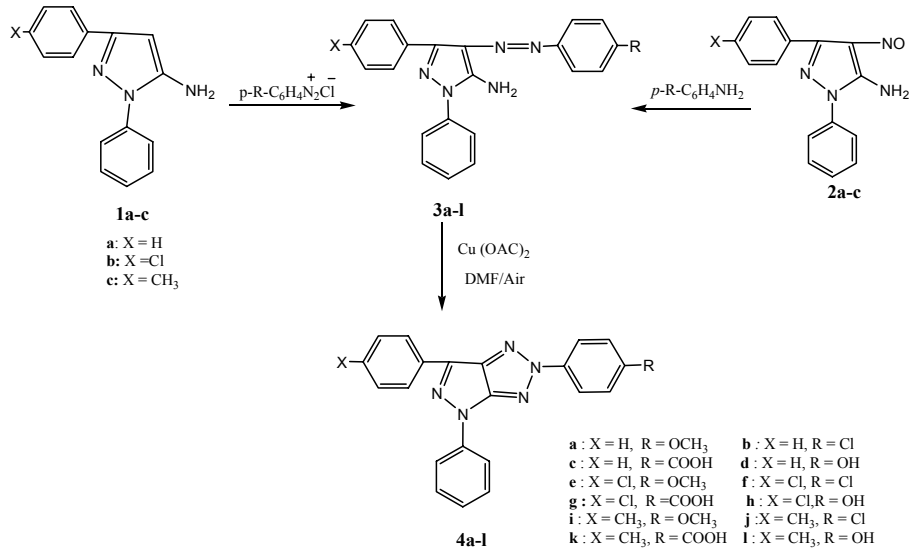
Keywords: Pyrazolo[4,3-*d*]-1,2,3-triazoles, *o*-Aminoazo compounds, Fluorescent properties, Fastness properties

INTRODUCTION

Pyrazoles are an interesting group of compounds because they have a broad spectrum pharmacologically properties such as antibacterial,[1] antihyperglycemice analgesic,[2] antiparasitic,[3] antimicrobial[4] and antischistosomal activities.[5] The pyrazole synthesis of particular use because there are themselves building block for a variety of pyrazole containing structure such as pyrazoloisoquinolines,[6] pyrazolopyrimidines,[7] pyrazolopyridines,[8] pyrazolopyrazines[9] and pyrazolotriazoles.[10] Some azopyrazole derivatives have many applications in dyes.[11] As a part of our continuing interest in heterocyclic chemistry, we now report the successful synthesis of some new pyrazolotriazoles and fused pyrazolotriazole derivatives.

RESULTS AND DISCUSSION

The nitrosation of the 5-amino-1,3-diaryl-1*H*-pyrazoles **1a-c** was carried out according to the previously reported methods to give compounds **2a-c**.[12] The reaction of **2a-c** with aromatic amines gave the corresponding *o*-amino azo compounds **3a-l** in good yield. Also, 5-amino-1,3-diaryl-1*H*-pyrazoles **1a-c** coupled with aryl diazonium salts to yield 5-amino-4-arylazo-1,3-diaryl-1*H*-pyrazoles **3a-l** which on oxidation with cupric acetate in the presence of air gave 2,4,6-



***Scheme* 1**

***Table* 1.** Synthesis of substituted 2,4,6-triaryl-2,4-dihydropyrazole[4,3-*d*][1,2,3] triazoles **4a-l**

Entry	X	R	Yield (%)	mp (°C)
4a	H	OCH_3	91	210 - 212
4b	H	Cl	98	228 - 230
4c	H	COOH	95	338 - 340
4d	H	OH	90	189 - 190
4e	Cl	OCH_3	88	140 - 143
4f	Cl	Cl	90	199 - 200
4g	Cl	COOH	95	230 - 232
4h	Cl	OH	87	185 - 187
4i	CH_3	OCH_3	98	170 - 171
4j	CH_3	Cl	98	170 - 171
4k	CH_3	COOH	93	330 - 332
4l	CH_3	OH	85	195 - 197

***Table* 2.** Absorption and fluorescence emission spectral data of the compounds **4a-l**

Compound	Absorption max (nm)	Log ε	Fluorescence emission max (nm)	Φ_f
4a	330	4.14	430	0.0341
4b	360	4.74	446	0.0370
4c	360	4.08	441	0.1260
4d	360	4.28	430	0.0370
4e	360	5.36	443	0.0281
4f	390	4.69	452	0.00797
4g	360	4.58	430	0.0294
4h	360	4.36	430	0.0038
4i	360	5.08	441	0.0323
4j	360	4.11	451	0.0193
4k	370	4.25	444	0.0321
4l	370	4.37	431	0.0314

triaryl-6*H*-pyrazolo[3,4-*d*]-1,2,3-triazoles **4a-l** (*Scheme* 1) in good yield (*Table* 1). The ^{1}H NMR and IR spectra of **4a-l** showed the absence of an exchangeable singlet band and the vibrational frequency for the amino groups. The absorption and fluorescence emission spectra of compounds **4a-l** have been measured in DMF as a solvent, and the spectral data were collected in (*Table* 2). As can be seen the absorption spectra display strong bands (log ε_{max} range from 4.08 to 5.36) in the range from 330 to 390 nm, depending on the nature of substituent at the phenyl rings. Such behavior is characteristic for an allowed π-π* transition over the whole skeleton of the molecule. The fluorescence emission characteristics of the mentioned compounds **4a-l** have been also investigated. The spectra reveal blue to green emission (λ_{ex} = 330 - 490 nm) depending on the substituent group. The shift of the emission maximum shows no general trend, however, the emission maximum is red shifted on changing the substituent from Cl or COOH to OCH_3 or OH group in the case of monosubstituted compounds **4a-l** which is in agreement with the π-π* nature of the excited single state. The fluorescence quantum yield is also depending on the nature of substituent where Φ_f increases by introduction of an electron withdrawing group as can be seen from the value of **4a** and **4d**. In fact the Φ_f -value was markedly decreased when additional substituent was introduced on the co-axial phenyl groups. These results are in agreement with the previously reported data.[13]

The diazotization of compounds **1a-c** followed by cou-

***Table* 3.** Synthesis of substituted *o*-amino azo dyes **5a-f**

Entry	X	R^1	R^2	R^1R^2	Yield (%)	mp (^oC)
5a	H	H	CH_3		80	135 - 137
5b	H	-	-	benzo	75	165 - 167
5c	Cl	H	CH_3		87	145 - 155
5d	Cl	-	-	benzo	60	199 - 200
5e	CH_3	H	CH_3		50	134 - 136
5f	CH_3	-	-	benzo	80	144 - 147

***Table* 4.** Synthesis of substituted *5*-triazoly-1,3-diarylpyrazole derivatives **6a-f**

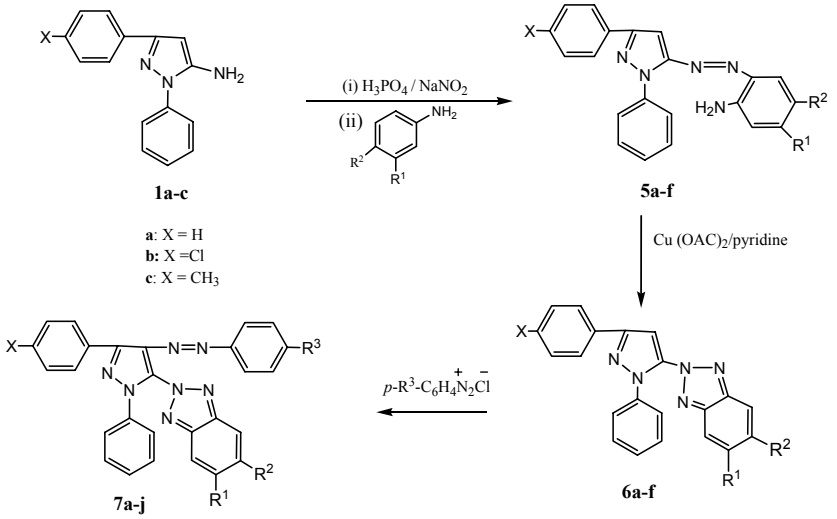
Entry	X	R^1	R^2	R^1R^2	Yield (%)	mp (^oC)
6a	H	H	CH_3	-	80	120 - 122
6b	H	-	-	benzo	75	148 - 150
6c	Cl	H	CH_3	-	83	142 - 145
6d	Cl	-	-	benzo	77	189 - 190
6e	CH_3	H	CH_3	-	75	120 - 121
5f	CH_3	-	-	benzo	80	130 - 132

pling with aryl amines gave the corresponding dyes **5a-f** in good yield (*Table* 3). The IR spectra of **5a-f** showed the azo groups (N=N) vibration frequencies at 1662 - 1675 cm^{-1} region, stretching vibrations for the amino group at 3275 - 3423 cm^{-1} region. The oxidation of *o*-aminoazo dyes gave 5-triazoly-1,3-diarylpyrazole derivatives **6a-f** in good yield

***Table* 5.** Synthesis of substituted 5-triazol-1,3-diaryl-4-arylazo pyrazole derivatives **7a-j**

Entry	X	R^1	R^2	R^1R^2	R^3	Yield (%)	mp (^oC)
7a	H	H	CH_3	-	OCH_3	69	130 - 132
7b	H	-	-	benzo	OCH_3	60	160 - 162
7c	H	H	CH_3	-	Cl	68	120 - 121
7d	Cl	H	CH_3	-	OCH_3	77	189 - 190
7e	Cl	-	-	benzo	OCH_3	77	125 - 128
7f	Cl	H	CH_3	-	Cl	73	130 - 132
7g	Cl	-	-	benzo	Cl	80	123 - 125
7h	CH_3	H	CH_3	-	OCH_3	60	115 - 117
7i	CH_3	-	-	benzo	OCH_3	75	125 - 127
7j	CH_3	-	-	benzo	Cl	75	120 - 122

(*Table* 4). The ^1H NMR spectra of compounds **6a-f** showed singlets within the region of 6.7 - 7.2 ppm due to CH proton of the pyrazole ring, a sharp singlets at δ = 2.1 - 2.3 ppm corresponding to CH_3 groups. Coupling of **6a-f** with aryl diazonium salts in ethanol, buffered with sodium acetate solution at pH = 6, gave the corresponding **7a-j** in good yield (*Table* 5). IR spectra of **7a-j** showed the azo groups (N=N) vibration frequencies at 1496 - 1596 cm^{-1} region. The ^1H NMR spectra of **7a-j** showed the absence of singlet signals at 6.6 - 6.8 ppm region corresponding for the CH proton of the pyrazole ring (*Scheme* 2).



a: X = H
b: X =Cl
c: X = CH_3

a : R^1 = H, X = H, R^2 = CH_3, R^3 = OCH_3
b: R^1R^2 = benzo, X = H, R^3 = OCH_3
c: R^1 = H, X = H, R^2 = CH_3, R^3 = Cl
d :R^1= H, X = Cl , R^2 =CH_3, R^3 = OCH_3
e :R^1R^2 = benzo, X= Cl, R^3= OCH_3
f : R^1 = H, X = Cl, R^2 =CH_3, R^3= Cl
g : R^1R^2 = benzo, X= Cl, R^3= Cl
h :R^1 = H, X = CH_3, R^2 = CH_3, R^3= OCH_3
i : R^1R^2 = benzo, X= CH_3, R^3 = OCH_3
j: R^1R^2 = benzo, X= CH_3, R^3 = Cl

a : R^1= H, X = H, R^2 = CH_3
b : R^1R^2 = benzo, X = H
c : R^1 = H, X = Cl, R^2 = CH_3
d: R^1 R^2 = benzo, X= Cl
e : R^1 = H, X = CH_3, R^2 = CH_3
f : R^1R^2 = benzo X = CH_3

***Scheme* 2**

It is worthy to mention that compounds **4a-l** have fluorescent properties due to the fused triazole ring to the pyrazole moiety, while compounds **6a-f** and **7a-j** have no fluorescent properties.

EXPERIMENTAL

Melting points were uncorrected. IR spectra were recorded on a Perkin-Elmer1430 spectrophotometer using KBr disk technique. ^{1}H-NMR spectra were measured on a Bruker AC spectrometer (300 MHz) in DMSO, in deuterated dimethylsulphoxide (DMSO-d_6) using tetramethylsilane (TMS) as the internal reference; chemical shifts were expressed in (δ) ppm. Standard electron impact mass spectra (EI) were obtained using a Finnigan MAT 8222 spectrometer at 70 eV. The electronic absorption spectra of the compounds **4a-l** have been measured by using Shimadzu 1301-PC spectrophotometer while their fluorescence spectra have been recorded on Perkin-Elmer L550B spectroflurometer. The measurements were done at room temperature using two matched quartz cuvettes. The fluorescence yield was measured relative to quinine bisulphate with an absorption maximum. Progress of reactions was monitored by the thin-layer chromatography (TLC) using benzene/ethyl acetate (9:1) as eluent.

Synthesis of 4-Arylazo-5-amino-1,3-diaryl-1*H*-pyrazoles (3a-l)

Method A: A mixture of 5-amino-1,3-diaryl-4-nitroso-1*H*-pyrazoles **2a-c** (1.5 mmol) and aromatic amines (1.9 mmol) in NaOH (50%; 1.8 mL) was refluxed for 5 h. The mixture was allowed to cool to room temperature and then, poured into crushed ice with vigorous stirring. The solid formed was filtered, washed with water several times and then dried.

Method B: The conversation of amino pyrazoles **1a-c** to 4-arylazo-5-amino-1,3-diaryl-1*H*-pyrazoles **3a-l** was carried out according to the previously reported method.[14]

General procedure of synthesis 2,4,6-triaryl-2,4-dihydropyrazole [4, 3-*d*] [1,2,3]triazoles (4a-l)

A solution of compounds **3a-l** (1.3 mmol) in 2.6 mL of pyridine was added to 0.14 g of cupric acetate (0.17 mmol) and the reaction mixture was refluxed for 7 h while a stream of air was bubbled in the reaction mixture. The reaction mixture was kept for 12 h at room temperature. The separated product was filtered, washed with ethanol, dried and recrystallizated from EtOH to give compounds **4a-l**.

2-(4-Methoxyphenyl)-4,6-diphenyl-2,4-dihydropyrazolo [4,3-*d*] [1,2,3]triazole (4a): IR (KBr) (ν_{max}, cm^{-1}): 3052, 2924; ^{1}H NMR; δ_H (ppm): 3.8 (s, 3H, OCH_3), 7.2-8.2 (m, 14H, ArH); Ms: 368 (M^+).

2-(4-Chlorophenyl)-4,6-diphenyl-2,4-dihydropyrazolo [4,3-*d*] [1,2,3] triazole (4b): IR (KBr) (ν_{max}, cm^{-1}): 3057, 2923; ^{1}H NMR; δ_H (ppm): 7.2-8.2 (m, 14H, ArH); Ms: 373 (M^++2).

4-(4,6-Diphenylpyrazolo [4,3-*d*] [1,2,3] triazol-2(4*H*)-yl) benzoic acid (4c): IR (KBr) (ν_{max}, cm^{-1}): 3051, 2923, 1695; ^{1}H NMR; δ_H (ppm): 7.05-8.5 (m, 14H, ArH), 13 (s, 1H, COOH); Ms: 381 (M^+).

4-(4,6-Diphenylpyrazolo [4,3-*d*] [1,2,3] triazol-2(4*H*)-yl) phenol (4d): IR (KBr) (ν_{max}, cm^{-1}): 3054, 2925; ^{1}H NMR; δ_H (ppm): 5.8 (s, 1H, OH), 7.2-8 (m, 14H, ArH); Ms: 353 (M^+).

6-(4-Dichlorophenyl)-2-(4-methoxyphenyl)-4-phenyl-2,4-dihydropyrazolo[4,3-*d*] [1,2,3] triazole (4e): IR (KBr) (ν_{max}, cm^{-1}): 3058, 2928; ^{1}H NMR; δ_H (ppm): 3.8 (s, 3H, OCH_3), δ 7.1-7.8 (m, 13H, ArH); Ms: 403 (M^++2).

2,6-Bis(4-chlorophenyl)-4-phenyl-2,4-dihydropyrazolo [4,3-*d*] [1,2,3] triazole (4f): IR (KBr) (ν_{max}, cm^{-1}): 3058, 2928; ^{1}H NMR; δ_H (ppm): 6.9-8.1 (m, 13H, ArH); Ms: 408 (M^++2).

4-[6-(4-Chlorophenyl)-4-phenylpyrazolo[4,3-*d*][1,2,3] triazol-2(4*H*)-yl]benzoic acid (4g): IR (KBr) (ν_{max}, cm^{-1}): 3060, 2924), 1600; ^{1}H NMR; δ_H (ppm): 7.05-8.5 (m, 13H, ArH), 12.5 (s, 1H, COOH); Ms: 417 (M^++2).

4-[6-(4-Chlorophenyl)-4-phenylpyrazolo[4,3-*d*][1,2,3] triazol-2(4*H*)-yl]phenol (4h): IR (KBr) (ν_{max}, cm^{-1}): 3059, 2922; ^{1}H NMR; δ_H (ppm): 5.8 (*s*, 1H, OH), 7.1-8.2 (m, 13H, Ar-H); Ms: 388 (M^++2).

2-(4-Methoxyphenyl)-4-phenyl-6-*p*-tolyl-2,4-dihydropyrazolo[4,3-*d*][1,2,3]triazole (4i): IR (KBr) (ν_{max}, cm^{-1}): 3056, 2919. ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 3.8 (s, 3H, OCH_3), 6.9-8.1 (m, 13H, ArH); Ms: 381 (M^+).

2-(4-Chlorophenyl)-4-phenyl-6-*p*-tolyl-2,4-dihydropyrazolo[4,3-*d*][1,2,3]triazole (4j): IR (KBr) (ν_{max}, cm^{-1}): 3048, 2920; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 6.7-8 (m, 13H, ArH); Ms: 387 (M^++2).

4-(4-Phenyl-6-*p*-tolylpyrazolo[4,3-*d*][1,2,3]triazole-2 (4*H*)-yl)benzoic acid (4k): IR (KBr) (ν_{max}, cm^{-1}): 3055, 2920,

1599; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 6.7-8.05 (m, 13H, ArH), 12.3 (s, 1H, COOH); Ms: 396 (M^+).

4-(4-Phenyl-6-*p*-tolylpyrazolo [4,3-*d*][1,2,3]triazole-2(4*H*)-yl) phenol (4l): IR (KBr) (ν_{max}, cm^{-1}): 3056, 2920; ^{1}H NMR; δ_H (ppm): 2.3(s, 3H, CH_3), 5.8 (s, 1H, OH), 6.7-8 (m, 13H, ArH); Ms: 367 (M^+).

General procedure for synthesis of *5*-triazoly-1,3-diaryl-pyrazole derivatives (6a-f)

Preparation of *o*-amino azo dye.

The appropriate 5-amino-1,3-diaryl-pyrazoles **1a-c** (4.3 mmol) was dissolved in 4.25 mL of phosphoric acid and then, cooled (0 ^oC). 0.85 mL of concentrated nitric acid was slowly added in portions (over 15 - 20 min). The reaction mixture was stirred for 30 - 40 min at 0 - 5 ^oC, and then, 0.64 g of sodium nitrite as a solid (9.3 mmol) was added slowly (over 30 - 45 min). The mixture was stirred for 1 h, at 0 - 5 ^oC and excess sodium nitrite was decomposed by addition of urea. The diazonium salt prepared was added to the appropriate aromatic amine (4.3 mmol) which dissolved in 2.5 mL of $NaHCO_3$ (25%), cooled to 0 - 5 ^oC and the pH was kept at 5 - 6 by the addition of sodium acetate. The reaction mixture was stirred for a further period of 3 - 3.5 h and the solid separated was filtered, washed with water and dried to give the *o*-amino azo dyes **5a-f**.

2-[(1,3-Diphenyl-1*H*-pyrazol-5-yl) diazenyl]-5-methyl-benenamine (5a): IR (KBr) (ν_{max}, cm^{-1}): 1663, 3396, 3057, 2928; Ms: 353 (M^+).

1-[(1,3-Diphenyl-1*H*-pyrazol-5-yl) diazenyl] naphthalene-2-amine (5b): IR (KBr) (ν_{max}, cm^{-1}): 1666, 3400, 3058, 2928; Ms: 390 (M^++1).

2-[(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)diazenyl]-5-methyl benzenamine (5c): IR (KBr) (ν_{max}, cm^{-1}): 1662, 3423, 3062, 2931; Ms: 389 (M^++2).

1-[(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl)diazenyl]naphthalene-2-amine (5d): IR (KBr) (ν_{max}, cm^{-1}): 1666, 3427, 3059, 2928; Ms: 425 (M^++2).

5-Methyl-2-[(1-phenyl-3-*p*-tolyl-1*H*-pyrazol-5-yl)diazenyl] benzenamine (5e): IR (KBr) (ν_{max}, cm^{-1}): 1675, 3275, 3027, 2926; Ms: 367 (M^+).

1-[(1-Phenyl-3-*p*-tolyl-1*H*-pyrazol-5-yl) diazenyl] naphthalene-2-amine (5f): IR (KBr) (ν_{max}, cm^{-1}): 1674, 3423, 3055, 2925, 3055; Ms: 403 (M^+).

Triazolyzation

A mixture of the appropriate o-amino azo dyes **5a-f** (4.3 mmol) and 0.28 g of cupric acetate (4.3 mmol) in 7 mL of pyridine was heated under reflux for 4 - 5 h, till the color of the dyes had disappeared. The reaction mixture was cooled to 0 - 5 ^oC and 28.3 mL of HCl (5%) was added with constant stirring. The solid formed was filtered, washed with water and dried. The solid was then dissolved in acetic acid (10 - 15 mL) and a small amount of Zn dust (4.3 mmol) was added, and the mixture was refluxed for 1 h. The reaction mixture was filtered while hot, and the filtrate was cooled and then added to ice-water mixture. The solid formed was filtered, washed with water, dried and recrystallized from ethanol to give compounds **6a-f**.

2-(1,3-Diphenyl-1*H*-pyrazol-5-yl)-5-methyl-2*H*-benzo[*d*][1,2,3]triazole (6a): IR (KBr) (ν_{max}, cm^{-1}): 3056, 2929; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 6.8 (s, 1H, CH), 7.2-8.5 (m, 13H, ArH); Ms: 351 (M^+).

2-(1,3-Diphenyl-1*H*-pyrazol-5-yl)-2*H*-naphtho [2, 3-*d*][1,2,3]triazole (6b): IR (KBr) (ν_{max}, cm^{-1}): 3056, 2929; ^{1}H NMR; δ_H (ppm): 6.8 (s, 1H, CH), 7.1-8.3 (m, 16H, ArH); Ms: 386 (M^+-1).

2-[3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl]-5-methyl-2*H*-benzo[*d*][1,2,3] triazole (6c): IR (KBr) (ν_{max}, cm^{-1}): 3057, 2935; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 6.8 (s, 1H, CH), 7-8.7 (m, 12H, ArH); Ms: 387 (M^++2).

2-[3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-5-yl]-2*H*-naphtho[2,3-*d*][1,2,3] triazole (6d): IR (KBr) (ν_{max}, cm^{-1}): 3057, 2927; ^{1}H NMR; δ_H (ppm): 6.7 (s, 1H, CH), 7.1-8.5 (m, 15H, ArH); Ms: 423 (M^++2).

5-Methyl-2-(1-phenyl-3-*p*-tolyl-1*H*-pyrazol-5-yl)-2*H*-benzo[*d*][1,2,3]triazole (6e): IR (KBr) (ν_{max}, cm^{-1}): 3060, 2928; ^{1}H NMR; δ_H (ppm): 2.1 (s, 3H, CH_3), 2.3 (s, 3H, CH_3) 7 (s, 1H, CH), 7.1-8.7 (m, 12H, ArH); Ms: 365 (M^+).

2-(1-Phenyl-3-*p*-tolyl-1*H*-pyrazol-5-yl)-2*H*-naphtho[2,3-*d*][1,2,3]triazole (6f): IR (KBr) (ν_{max}, cm^{-1}): 3055, 2924; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3) 6.8 (s, 1H, CH), 7.1-8.7 (m, 15H, ArH); Ms: 401 (M^+).

General procedure for synthesis of 5-triazol-1,3-diaryl-4-arylazopyrazole derivatives 7a-j

A solution of 0.11 g of sodium nitrite (1.6 mmol) was gradually added to a cold solution of an aromatic amine (1.6 mmol) in 0.5 mL of conc. HCl. The diazonium salt obtained was added with continuous stirring to a cold of compounds **6a-f** (1 mmol) in 4.9 mL of ethanol containing sodium acetate. The reaction mixture was stirred at 0 °C for 2 h. The solid obtained was filtered, washed with water and crystallized from ethanol to give compounds **7a-j**.

1-(4-Methoxyphenyl)-2-(5-(5-methyl-2*H*-benzo[*d*][1,2,3]triazol-2-yl)-1,3-diphenyl-1*H*-pyrazol-4-yl) diazene (7a): IR (KBr) (ν_{max}, cm^{-1}): 3058, 2927, 1600; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 3.7 (s, 3H, OCH_3), 6.1-8.2 (m, 17H, ArH); Ms: 485 (M^+).

1-(5-(2*H*-naphtho[2,3-d][1,2,3]triazol-2-yl)-1,3-diphenyl-1*H*-pyrazol-4-yl)-2-(4-methoxyphenyl)diazene (7b): IR (KBr) (ν_{max}, cm^{-1}): 3060, 2927, 1600; ^{1}H NMR; δ_H (ppm): 3.8 (s, 3H, OCH_3), 6.6-8.8 (m, 20H, ArH); Ms: 521 (M^+).

1-(4-Chlorophenyl)-2-[5-(5-methyl-2*H*-benzo[*d*][1,2,3]triazol-2-yl]-1,3-diphenyl-1*H*-pyrazol-4-yl)diazene (7c): IR (KBr) (ν_{max}, cm^{-1}): 3059, 2925, 1597; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 7-8.9 (m, 17H, ArH); Ms: 491 (M^++2).

1-[3-(4-Chlorophenyl)-5-(5-methyl-2*H*-benzo[*d*][1,2,3]triazol-2-yl]-1-phenyl-1*H*-pyrazol-4-yl)-2-(4-methoxyphenyl)diazene (7d): IR (KBr) (ν_{max}, cm^{-1}): 3058, 2928, 1598; ^{1}H NMR; δ_H (ppm): 2 (s, 3H, CH_3), 3.8 (s, 3H, OCH_3), 7-8 (m, 16H, ArH); Ms: 521 (M^++2).

1-[3-(4-Chlorophenyl)-5-(2*H*-naphtho[2,3-*d*][1,2,3]triazol-2-yl]-1-phenyl-1*H*-pyrazol-4-yl)-2-(4-methoxyphenyl) diazene (7e): IR (KBr) (ν_{max}, cm^{-1}): 3056, 2928, 1597; ^{1}H NMR; δ_H (ppm): 3.79 (*s*, 3H, OCH_3), 7.5-8 (*m*, 19H, Ar-H); Ms: 558 (M^++2).

1-(4-Chlorophenyl)-2-(3-(4-chlorophenyl)-5-(5-methyl-2*H*-benzo[*d*][1,2,3]triazol-2-yl)-1-phenyl-1*H*-pyrazol-4-yl)diazene (7f): IR (KBr) (ν_{max}, cm^{-1}): 3060, 2926, 1599; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 7-8.7 (m, 16H, Ar-H); Ms: 526 (M^++2).

1-(4-Chlorophenyl)-2-(3-(4-chlorophenyl)-5-(2H-naphtho[2,3-*d*][1,2,3]triazol-2-yl)-1-phenyl-1*H*-pyrazol-4-yl) diazene (7g): IR (KBr) (ν_{max}, cm^{-1}): 3059, 2928, 1698; ^{1}H NMR; δ_H (ppm): 7-8.35 (m, 19H, Ar-H); Ms: 562 (M^++2).

1-(4-Methoxyphenyl)-2-[5-(5-methyl-2*H*-benzo[*d*][1,2,3]triazol-2-yl)-1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl]diazene (7h): IR (KBr) (ν_{max}, cm^{-1}): 3024, 2925, 1598; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 3.7 (s, 3H, OCH_3), 7-8.35 (m, 16H, Ar-H); Ms: 489 (M^+).

1-[5-(2*H*-Naphtho[2,3-d][1,2,3]triazol-2-yl)-1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl]-2-(4-methoxyphenyl)diazene (7i): IR (KBr) (ν_{max}, cm^{-1}): 3055, 2924, 1598; ^{1}H NMR; δ_H (ppm): 2.3 (s, 3H, CH_3), 3.7 (s, 3H, OCH_3), 6.6-7.9 (m, 19H, ArH); Ms: 535 (M^+).

1-[5-(2*H*-Naphtho[2,3-d][1,2,3]triazol-2-yl)-1-phenyl-3-*p*-tolyl-1*H*-pyrazol-4-yl]-2-(4-chlorophenyl)diazene (7j): IR (KBr) (ν_{max}, cm^{-1}): 3056, 2925, 1598; ^{1}H NMR; δ_H (ppm): 2.2 (s, 3H, CH_3), 6.6-8.4 (m, 19H, ArH); Ms: 542 (M^++2).

Dyeing of Polyester Fabrics and Dyeing Properties

The prepared azo dyes **7a-j** was applied to polyester fiber. The dyeing procedure[14,15] and color fastness to light, washing, perspiration, and rubbing of the prepared dyes on fibers

***Table* 6.** Fastness properties[a] of dyes **7a-j** on polyester fabrics[b]

Dye	Colour	Washing		Perspiration		Rubbing		Sublimation		Light
		PES	Cotton	PES	Cotton	Dry	Wet	PES	Cotton	
7a	Light brown	3	3-4	3-4	3-4	3	3	3-4	4	4-5
7b	Brown	3-4	3-4	3-4	3-4	3	3	3	3-4	4-5
7c	Lemon Yellow	3	3	3-4	3-4	3-4	3-4	3-4	3-4	4-5
7d	Dark brown	3-4	3	3	3	4-5	4	4	4	4
7e	Light brown	3-4	3-4	3	3-4	4	3-4	3-4	3	4
7f	Light Begg	3	3-4	3-4	3-4	4-3	3-4	3-4	3	4-5
7g	Brown	3-4	3	3-4	3-4	3-4	3-4	4	3-4	4-5
7h	Dark Begg	3-4	3	3-4	3-4	3-4	3-4	4	4	4-5
7i	brown	3-4	3-4	3-4	3-4	3-4	3-4	4	4	4-5
7j	Light brown	3-4	3	3-4	3-4	4	3-4	3	3-4	4-5

[a]Rate for light fastness: 4-5 (acceptable), 1-3 (not acceptable); rate for different fastness: 3-4 (acceptable), 1-2 (not acceptable). [b]PES: Polyester

were studied using standard methods for the assessment of color fastness of textile (the *grey* scale).[16] The results obtained are shown in (*Table* 6). The results revealed that these dyes have good fastness properties. In conclusion, a set of ten useful disperse dyes **7a-j** were synthesized by azo coupling. The dyes were investigated for their dyeing characteristics on polyester and showed moderate to good (3-4) washing, perspiration, sublimation and rubbing fastness dry and wet. The light fastness of dyed exhibit good (4-5) fastness properties.

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