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Novel heterocyclic disazo dyes containing pyrazole and phenylpyrazole. part 1: Synthesis, characterization, solvent polarity and acid-base sensitive characteristics

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ABSTRACT

A series of diazotised aniline and aniline derivative compounds were reacted with solution of malononitrile in pyridine at 0–5 °C were obtained **1a-1m** compounds. Then 4-arylazo-3,5-diamino-1H-pyrazole **(2a-2m)** derivatives were synthesized by coupling arylazo malononitrile compounds with hydrazine. Finally, the synthesized pyrazole derivative **2a-2m** compounds were again diazotised. By reacting these diazotised compounds with 3-amino-5–hydroxy-1-phenylpyrazole, the new thirteen heterocyclic disazo dyes **(3a-3m)** were joined the dye literature and the dye industry. The structures of these newly synthesized compounds were characterized using elemental analysis and spectroscopic methods such as Fourier transform infrared spectroscopy-Attenuated total reflectance (FT-IR-ATR), ^{1}H-Nuclear magnetic resonance (^{1}H NMR) spectroscopy and mass spectroscopy. Then solvatochromic properties and solvent effect in dimethyl sulfoxide, dimethyl formamide, acetonitrile, acetic acid, methanol and chloroform were investigated. In addition, the effects of organic and inorganic acids and bases on the absorption spectra of the compounds and the substituent effect of the phenyl ring-bound groups were investigated.

1. Introduction

The synthesis of azo dyestuffs have great importance nowadays due to their many features such as having a wide color range from greenish yellow to turquoise, showing good fastness properties, being easily obtained from cheap starting materials, high dyeing ability and chromophoric strength [1,2].

In particularly, the presence of a heterocyclic atom such as nitrogen, oxygen, sulfur in the azo compounds allowed these dyes to show better fastness properties, to obtain not only from yellow to turquoise but also blue colors and to be used as a pH indicator in the presence of conjugated acid and base [3–7].

The growing interest in amino pyrazole and amino phenyl pyrazole compounds today is due to the ability to re-diazotised of these compounds, to obtain different heterocyclic dyes by reacted with various active methylene compounds and there can be used in different areas [8,9]. In recent years, amino pyrazole derivatives are preferred more in the textile and dyestuffs industry because they have a wide range of colors, high dyeing properties and permanent fastness properties [10–12]. Metal complexes of these compounds are also included in the literature with their ion selective properties [13,14].

Amino pyrazole derivatives are important compounds with a wide range of interesting properties [15,16], including antihyperglycemic [17], anti-inflammatory [18], antipyretic [19], antibacterial [20] and anti-microbial [21]. Also these compounds are used anti-fungal [22], anti-cancer [23,24], antiviral [25], antitubercular [26], antidiabetic [27] and antitumor agent [28]. Recently, studies have been conducted stating that some amino pyrazoles have anti-Alzheimer's inhibitory activity [29]. Due to these features, they have a widespread use in the field of biology, pharmacology and medicine due to their versatile biological activities.

In addition, the amino azo pyrazole derivative dyes are widely used in various and current applications such as metallochromic indicators [30], optical data storage tools [31], nonlinear optical systems [32], dye-sensitized solar cells [33], organic light emitting diodes [34], LCD color filters and coloring of plastics and polymer [35,36]. These compounds are frequently used in organic advanced synthesis applications.

In the present study, firstly, 13 novels amino pyrazole derivatives heterocyclic disazo dyestuffs (**3a-3m**) having industrial significance in bright colors were synthesized by reacting diazotised pyrazole derivative **2a-2m** compounds with 3-amino-5–hydroxy-1-phenylpyrazole. Then, characteristic features were clarified by methods such as FT-IR spectroscopy, ^{1}H NMR spectroscopy, mass spectroscopy and elemental analysis. Lastly, tautomeric properties,

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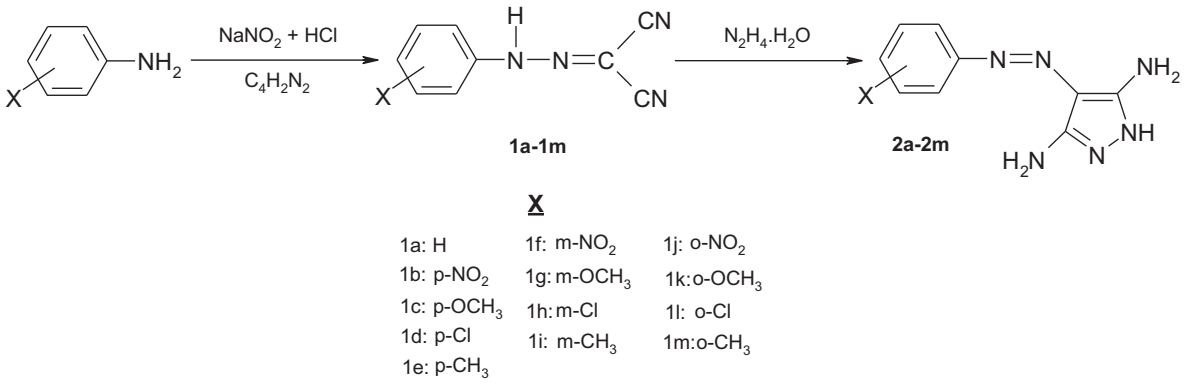


Scheme 1. General synthesis method of dyes **2a-2m**.

absorbance properties and substituent effects of these compounds in 6 different solvents and acid-base solutions were investigated using UV–Vis. spectroscopy.

2. Experimental

2.1. Materials and methods

The chemicals used in the experiments were supplied from Merck, Acros and Sigma-aldrich companies. These chemicals were used in their original form with high purity.

Melting points of dyestuffs were determined using the Electrothermal 9100 apparatus. Elemental analysis was calculated by Costech ECS 4010 analyzer device. IR spectral data were measured using a Perkin Elmer UATR Two (FT-IR) Spectrophotometer device. The mass spectrum values of the synthesized dyestuffs were determined using the Thermo Scientific TSQ Quantum Access MAX instrument. The data of the ^{1}H NMR spectra were determined by the Bruker-Spectrospin Avance DPX 400 Ultra-Shield device in DMSO–d_6 solvent utilizing the tetramethylsilane as the referans compound, and chemical shifts (δ) were recorded as ppm. UV–Vis. spectrums were procured by PG T80+ high performance double beam spectrophotometer in six different solvents such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), acetonitrile (CH_3CN), methanol (CH_3OH), acetic acid (CH_3CO_2H) and chloroform ($CHCl_3$) at concentration 1×10^{-6} M.

2.2. Synthesis of 4-arylazo-3,5-diamino-1H-pyrazoles (2a-2m)

1a-1m and **2a-2m** dyes were synthesized following the method given in reference of [37]. The general synthesis method of **1a-1m** and **2a-2m** were presented in Scheme 1.

2.3. Synthesis of new heterocyclic disazo dyestuffs (3a-3m)

2.3.1. 4-(3′-amino-4′-phenylazo-1′H-pyrazole-5′-ylazo)−3-amino-5–hydroxy-1-phenylpyrazole (3a)

4-phenylazo-3,5-diamino-1H-pyrazole compound **(2a)** (1.0 g, 2.58 mmol) was dissolved in a mixture of glacial acetic acid and concentrated hydrochloric acid (30 ml, ratio 1: 1) and the solution was cooled to 0–5 °C. While the solution was stirring, $NaNO_2$ (3.87 mmol) in water (10 ml) was slowly added to this solution. Stirring was continued until the diazonium salt was formed (2 h). Then the basic mixed solution of 3-amino-5–hydroxy-1-phenylpyrazole (0.45 g, 2.58 mmol) with potassium hydroxide (0.14 g, 2.58 mmol) and water (20 ml) was added to the obtained diazonium salt. The reaction was stirred for a further 4 h under cold conditions (0–5 °C). At the end of the reaction, the synthesized dye 3a was precipitated with 50 ml of water, filtered, washed in water many times (60 ml). Later the dye was dried and crystallized from the DMF-water (1:2, v:v) mixture. Color: red crystals, yield: 80%, mp: 321–322 °C, mw: 388 g/mol, MS *m/z*: 388.51 (M^+), Elemental analysis: Calculated for $C_{18}H_{16}N_{10}O$: C, 55.67; H, 4.12; N, 36.08%; Found: C, 55.68; H, 4.18; N, 36.21%.

2.3.2. 4-[3′-amino-4′-(p-nitrophenylazo)−1′H-pyrazole-5′-ylazo]−3-amino-5–hydroxy-1-phenyl pyrazole (3b)

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′-*amino*-4′-(*p-nitrophenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3b**) was obtained from 4-(p-nitrophenylazo)−3,5-diamino-1H-pyrazole (**2b**) (1 g, 2.31 mmol). Color: brown crystals, yield: 92%, mp: 341–342 °C, mw: 433 g/mol, MS *m/z*: 432.70 (M^+), Elemental analysis: Calculated for $C_{18}H_{15}N_{11}O_3$: C, 49.88; H, 3.46; N, 35.57%; Found: C, 49.95; H, 3.54; N, 35.48%.

2.3.3. 4-[3′-amino-4′-(p-methoxyphenylazo)−1′H-pyrazole-5′-ylazo]−3-amino-5–hydroxy-1-phenyl pyrazole (3c)

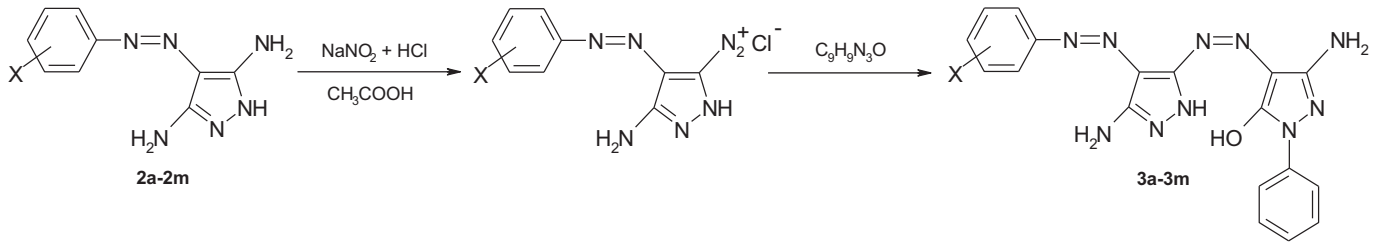
Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′-*amino*-4′-(*p-methoxyphenylazo*-1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3c**) was obtained from 4-(p-methoxyphenylazo)−3,5-diamino-1H-pyrazole (**2c**) (1 g, 2.39 mmol). Color: orange crystals, yield: 76%, mp: 327–328 °C, mw: 418 g/mol, MS *m/z*: 418.02 (M^+), Elemental analysis: Calculated for $C_{19}H_{18}N_{10}O_2$: C, 54.54; H, 4.30; N, 33.49%; Found: C, 54.50; H, 4.39; N, 33.48%.

2.3.4. 4-[3′-amino-4′-(p-chlorophenylazo)−1′H-pyrazole-5′-ylazo]−3-amino-5–hydroxy-1-phenyl pyrazole (3d)

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′-*amino*-4′-(*p-chlorophenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3d**) was obtained from 4-(p-chlorophenylazo)−3,5-diamino-1H-pyrazole (**2d**) (1 g, 2.37 mmol). Color: brown crystals, yield: 86%, mp: 331–332 °C, mw: 422.5 g/mol, MS *m/z*: 421.98 (M^+), Elemental analysis: Calculated for $C_{18}H_{15}ClN_{10}O$: C, 51.12; H, 3.55; N, 33.14%; Found: C, 51.18; H, 3.61; N, 33.20%.

2.3.5. 4-[3′-amino-4′-(p-methylphenylazo)−1′H-pyrazole-5′-ylazo]−3-amino-5–hydroxy-1-phenyl pyrazole (3e)

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′-*amino*-4′-(*p-methylphenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3e**) was obtained from 4-(p-methylphenylazo)−3,5-diamino-1H-pyrazole (**2e**) (1 g,



Scheme 2. General synthesis method of dyes **3a-3m**.

2.49 mmol). Color: orange crystals, yield: 79%, mp: 292–293 °C, mw: 402 g/mol, MS *m/z*: 402.08 (M^+), Elemental analysis: Calculated for $C_{19}H_{18}N_{10}O$: C, 56.72; H, 4.48; N, 34.83%; Found: C, 56.78; H, 4.55; N, 34.88%.

2.3.6. 4-[3′-amino-*4′-(*m-nitrophenylazo*)−1′H-pyrazole-5′-*ylazo*]−3-amino-5–hydroxy-1-phenyl pyrazole (3f)*

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′*-amino-*4′-(*m-nitrophenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3f**) was obtained from 4-(m-nitrophenylazo)−3,5-diamino-1H-pyrazole (**2f**) (1 g, 2.31 mmol). Color: brown crystals, yield: 89%, mp: 301–302 °C, mw: 433 g/mol, MS *m/z*: 432.74 (M^+), Elemental analysis: Calculated for $C_{18}H_{15}N_{11}O_3$: C, 49.88; H, 3.46; N, 35.57%; Found: C, 49.90; H, 3.52; N, 35.49%.

2.3.7. 4-[3′-amino-*4′-(*m-methoxyphenylazo*)−1′H-pyrazole-5′-*ylazo*]−3-amino-5–hydroxy-1-phenyl pyrazole (3g)*

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′*-amino-*4′-(*m-methoxyphenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3g**) was obtained from 4-(m-methoxyphenylazo)−3,5-diamino-1H-pyrazole (**2g**) (1 g, 2.39 mmol). Color: orange crystals, yield: 73%, mp: 305–306 °C, mw: 418 g/mol, MS *m/z*: 418.10 (M^+), Elemental analysis: Calculated for $C_{19}H_{18}N_{10}O_2$: C, 54.54; H, 4.30; N, 33.49%; Founded: C, 54.49; H, 4.33; N, 33.45%.

2.3.8. 4-[3′-amino-*4′-(*m-chlorophenylazo*)−1′H-pyrazole-5′-*ylazo*]−3-amino-5–hydroxy-1-phenyl pyrazole (3h)*

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′*-amino-*4′-(*m-chlorophenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3h**) was obtained from 4-(m-chlorophenylazo)−3,5-diamino-1H-pyrazole (**2h**) (1 g, 2.37 mmol). Color: brown crystals, yield: 84%, mp: 310–311 °C, mw: 422.5 g/mol, MS *m/z*: 422.04 (M^+), Elemental analysis: Calculated for $C_{18}H_{15}ClN_{10}O$: C, 51.12; H, 3.55; N, 33.14%; Founded: C, 51.19; H, 3.54; N, 33.16%.

2.3.9. 4-[3′-amino-*4′-(*m-methylphenylazo*)−1′H-pyrazole-5′-*ylazo*]−3-amino-5–hydroxy-1-phenyl pyrazole (3i)*

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′*-amino-*4′-(*m-methylphenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3i**) was obtained from 4-(m-methylphenylazo)−3,5-diamino-1H-pyrazole (**2i**) (1 g, 2.49 mmol). Color: red crystals, yield: 76%, mp: 317–318 °C, mw: 402 g/mol, MS *m/z*: 402.15 (M^+), Elemental analysis: Calculated for $C_{19}H_{18}N_{10}O$: C, 56.72; H, 4.48; N, 34.83%; Founded: C, 56.81; H, 4.57; N, 34.84%.

2.3.10. 4-[3′-amino-*4′-(*o-nitrophenylazo*)−1′H-pyrazole-5′-*ylazo*]−3-amino-5–hydroxy-1-phenyl pyrazole (3j)*

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′*-amino-*4′-(*o-nitrophenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3j**) was obtained from 4-(o-nitrophenylazo)−3,5-diamino-1H-pyrazole (**2j**) (1 g, 2.31 mmol). Color: brown crystals, yield: 88%, mp: 338–339 °C, mw: 433 g/mol, MS *m/z*: 432.68 (M^+), Elemental analysis: Calculated for $C_{18}H_{15}N_{11}O_3$: C, 49.88; H, 3.46; N, 35.57%; Founded: C, 49.81; H, 3.45; N, 35.53%.

2.3.11. 4-[3′-amino-*4′-(*o-methoxyphenylazo*)−1′H-pyrazole-5′-*ylazo*]−3-amino-5–hydroxy-1-phenyl pyrazole (3k)*

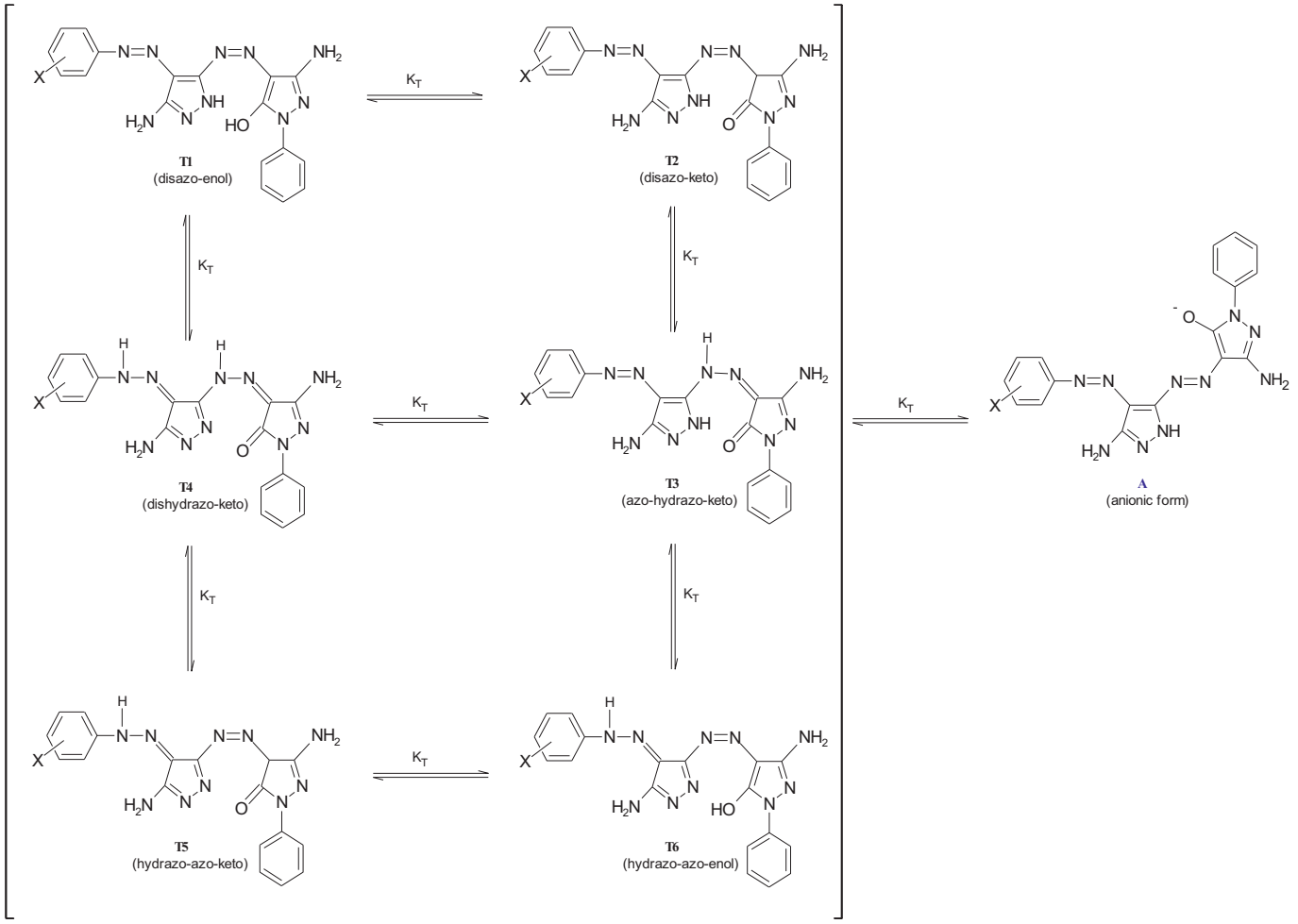
Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3-*amino-*4′-(*o-methoxyphenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3k**) was obtained from 4-(o-methoxyphenylazo)−3,5-diamino-1H-pyrazole (**2k**) (1 g, 2.39 mmol). Color: orange crystals, yield: 71%, mp: 319–320 °C, mw: 418 g/mol, MS *m/z*: 418.06 (M^+), Elemental analysis: Calculated for $C_{19}H_{18}N_{10}O_2$: C, 54.54; H, 4.30; N, 33.49%; Founded: C, 54.57; H, 4.37; N, 33.42%.

2.3.12. 4-[3′-amino-*4′-(*o-chlorophenylazo*)−1′H-pyrazole-5′-*ylazo*]−3-amino-5–hydroxy-1-phenyl pyrazole (3l)*

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′*-amino-*4′-(*o-chlorophenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3l**) was obtained from 4-(o-chlorophenylazo)−3,5-diamino-1H-pyrazole (**2l**) (1 g, 2.37 mmol). Color: brown crystals, yield: 81%, mp: 328–329 °C, mw: 422.5 g/mol, MS *m/z*: 422.09 (M^+), Elemental analysis: Calculated for $C_{18}H_{15}ClN_{10}O$: C, 51.12; H, 3.55; N, 33.14%; Founded: C, 51.15; H, 3.54; N, 33.18%.

2.3.13. 4-[3′-amino-*4′-(*o-methylphenylazo*)−1′H-pyrazole-5′-*ylazo*]−3-amino-5–hydroxy-1-phenyl pyrazole (3m)*

Using the same procedure mentioned above for the synthesis of dye **3a**, 4-[3′*-amino-*4′-(*o-methylphenylazo*)−1′H-*pyrazole*-5′-*ylazo*]−3-amino-5–hydroxy-1-phenylpyrazole (**3m**) was obtained from 4-(o-methylphenylazo)−3,5-diamino-1H-pyrazole (**2m**) (1 g, 2.49 mmol). Color: red crystals, yield: 74%, mp: 313–314 °C, mw: 402 g/mol, MS *m/z*: 402.11 (M^+), Elemental analysis: Calculated for $C_{19}H_{18}N_{10}O$: C, 56.72; H, 4.48; N, 34.83%; Founded: C, 56.71; H, 4.43; N, 34.84%. The general synthesis method of 3**a-3m** was presented in Scheme 2.



Scheme 3. Possible tautomeric structures of **3a-3m** dyes.

3. Results and discussion

3.1. FT-IR spectral evaluation and possible tautomeric structures of new 3a-3m dyes

3a-3m compounds could be found 6 possible tautomeric forms such as **T1** (disazo-enol), **T2** (disazo-keto), **T3** (azo-hydrazo-keto), **T4** (dishydrazo-keto), **T5** (hydrazo-azo-keto) and **T6** (hydrazo-azo-enol). These tautomeric forms were shown in Scheme 3.

The FT-IR spectrum of compounds provides an important gain in obtaining information about the presence or absence of compound-specific functional groups, especially in organic compounds. When comparing FT-IR samples, it gives specific results for the fingerprint area, as well as the functional groups.

FT-IR spectrum data of the synthesized dyestuffs were given in Table 1. As an example, the FT-IR spectrum of dye 3j was given in Fig. 1.

As seen in Table 1, it was thought that the peaks seen in the range of 3393–3485 cm^{-1} belong to the amino (-NH_2) group attached to the phenyl pyrazole ring and the peaks seen at 3296–3380 cm^{-1} belong to the amino (-NH_2) group connected to the pyrazole ring. It was observed that the peaks in the range of 3158–3184 cm^{-1} belong to the imino (-NH) group attached to the pyrazole ring and the peaks between 1622 and 1657 cm^{-1} belong to the carbonyl (-C=O) group. The peaks observed between 1508 and 1557 and 1448–1498 cm^{-1} belong to the azo groups found in the structure of our compound.

Table 1
FT-IR spectral data of **3a-3m** dyes.

Dye No	Vibratioanal frequencies (cm^{-1})					
	ν_{NH2}	ν_{NH}	ν_{Ar-H}	ν_{Al-H}	$\nu_{C=O}$	$\nu_{N=N}$
3a	3442, 3317	3172	3061, 3021	–	1622	1537, 1497
3b	3485, 3380	3174	3066, 3028	–	1622	1508, 1498
3c	3418, 3296	3166	3069, 3024	2966	1627	1539, 1497
3d	3393, 3327	3173	3064, 3022	–	1630	1551, 1448
3e	3414, 3309	3159	3058, 3016	2922	1633	1556, 1497
3f	3441, 3318	3158	3073, 3028	–	1624	1520, 1489
3g	3438, 3385	3162	3071, 3031	2922	1637	1533, 1498
3h	3423, 3311	3184	3064, 3024	–	1643	1538, 1498
3i	3443, 3312	3167	3062, 3026	2917	1657	1538, 1495
3j	3468, 3300	3170	3080, 3028	–	1650	1522, 1497
3k	3409, 3302	3178	3066, 3025	2923	1622	1538, 1497
3l	3443, 3305	3167	3060, 3019	–	1627	1540, 1498
3m	3441, 3314	3182	3066, 3022	2988	1627	1557, 1497

All of the IR spectra were taken while the dyes were solid. The appearance of two different amino (-NH_2) peaks, two different azo (-N=N) peaks and one carbonyl (-C=O) peak in the FT-IR spectrum results for all compounds showed that our dyes were in disazo-keto (**T2**) tautomeric form in solid phase.

3.2. ^{1}H NMR analysis and possible tautomeric structures of dyes

^{1}H NMR results of compounds were taken in DMSO solvent utilizing TMS as the internal reference. The measured values were

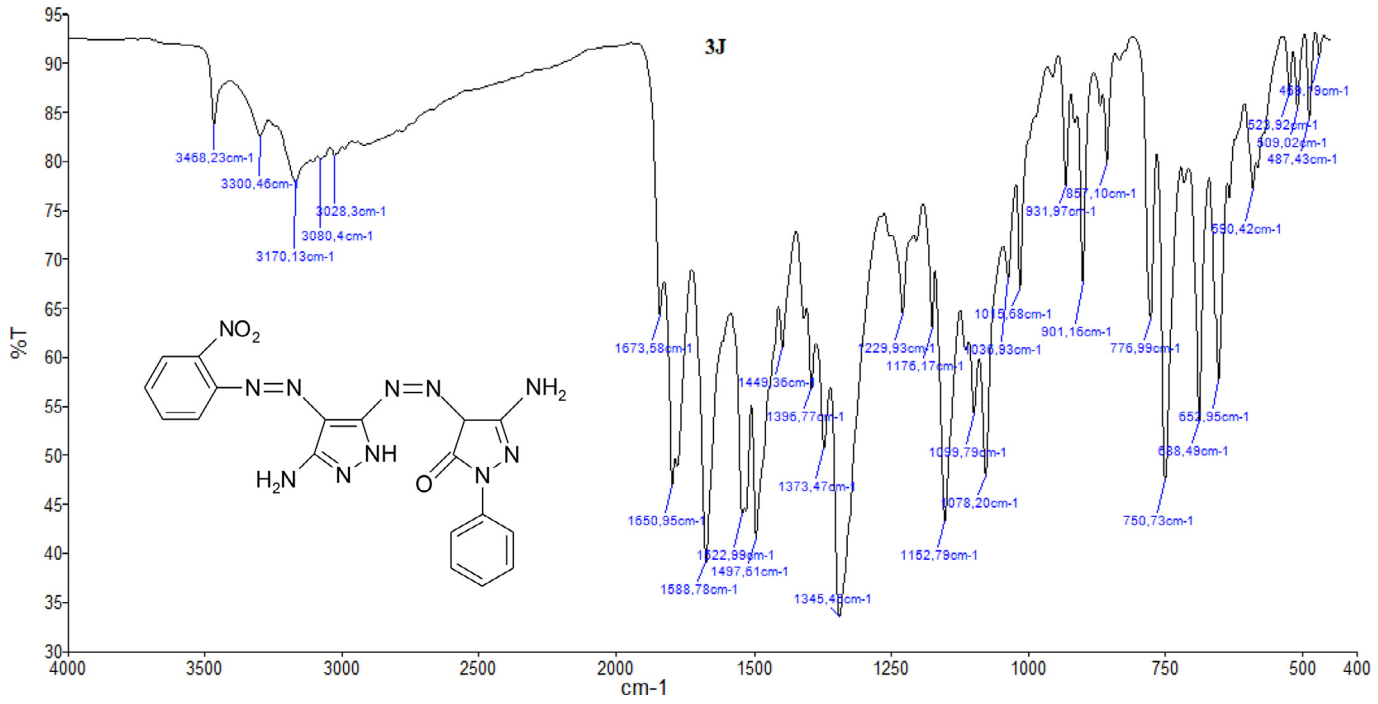


Fig. 1. FT-IR spectra of dye **3j.**

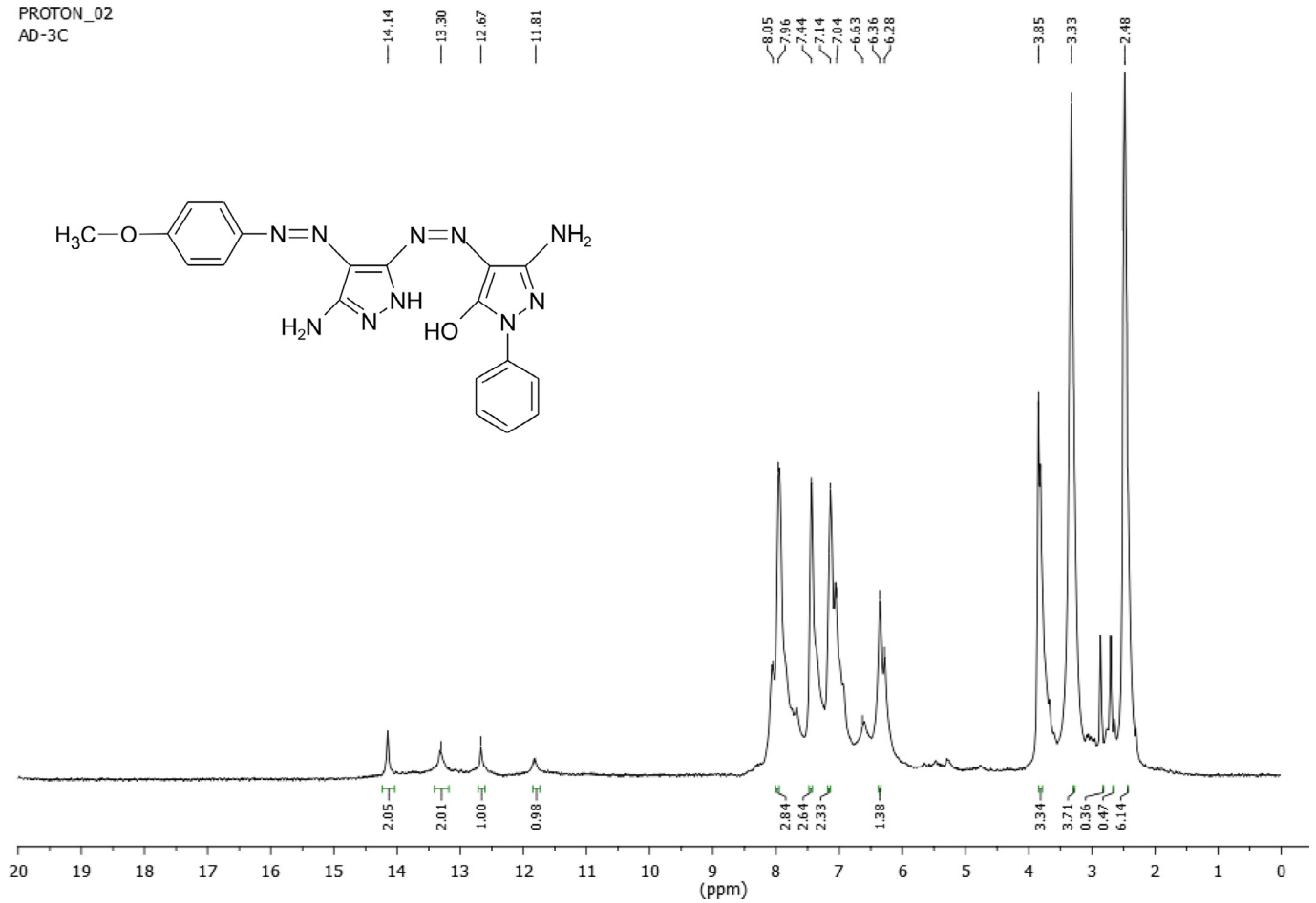


Fig. 2. ^{1}H NMR spectra of dye **3c**.

Table 2
Spectral data for ^{1}H NMR analyses of the synthesized dyes **3a-3m**.

^{1}H NMR[a] [(δ, ppm) (in DMSO–d_6)]						
Dye No	Phenylpyrazole-NH_2	Pyrazole-NH_2	Pyrazole-NH	Phenylpyrazole-OH	Aromatic-H	Aliphatic-H
3a	14.17 (s, 2H)	13.99 (s, 2H)	12.76 (s, 1H)	11.86 (s, 1H)	6.30–8.10 (m, 10H)	–
3b	14.09 (s, 2H)	13.45 (s, 2H)	12.78 (s, 1H)	12.03 (s, 1H)	6.22–8.32 (m, 9H)	–
3c	14.14 (s, 2H)	13.90 (s, 2H)	12.67 (s, 1H)	11.81 (s, 1H)	6.28–8.05 (m, 9H)	3.85 (s, 3H)
3d	14.17 (s, 2H)	13.80 (s, 2H)	12.77 (s, 1H)	11.86 (s, 1H)	6.29–8.10 (m, 9H)	–
3e	14.06 (s, 2H)	13.93 (s, 2H)	12.69 (s, 1H)	11.82 (s, 1H)	6.15–7.94 (m, 9H)	2.33 (s, 3H)
3f	14.31 (s, 2H)	13.74 (s, 2H)	12.78 (s, 1H)	11.94 (s, 1H)	6.14–8.05 (m, 9H)	–
3g	14.11 (s, 2H)	13.82 (s, 2H)	12.76 (s, 1H)	11.86 (s, 1H)	6.31–7.94 (m, 9H)	3.88 (s, 3H)
3h	14.12 (s, 2H)	13.62 (s, 2H)	12.79 (s, 1H)	11.89 (s, 1H)	6.27–7.98 (m, 9H)	–
3i	14.09 (s, 2H)	13.60 (s, 2H)	12.71 (s, 1H)	11.84 (s, 1H)	6.30–7.97 (m, 9H)	2.38 (s, 3H)
3j	14.25 (s, 2H)	13.42 (s, 2H)	12.69 (s, 1H)	11.89 (s, 1H)	6.31–8.10 (m, 9H)	–
3k	14.29 (s, 2H)	13.64 (s, 2H)	12.72 (s, 1H)	11.93 (s, 1H)	6.35–7.92 (m, 9H)	3.93 (s, 3H)
3l	14.21 (s, 2H)	13.56 (s, 2H)	12.84 (s, 1H)	11.73 (s, 1H)	6.40–7.93 (m, 9H)	–
3m	14.19 (s, 2H)	13.62 (s, 2H)	12.76 (s, 1H)	11.80 (s, 1H)	6.40–8.37 (m, 9H)	2.30 (s, 3H)

[a] Abbreviations: s; singlet, m; multiplet.

Table 3
UV–Vis. wavelength parameters (λ_{max}) of dyes **3a-3m** in various solvents.

Dye No	DMSO	DMF	Acetonitrile	Acetic acid	Methanol	Chloroform
3a	504, 410	500, 414	414	410	414	414
3b	538, 422	526, 422	422	362	366	426
3c	518, 424	506, 420	422	426	422	420
3d	538, 420	538, 424	420	362	366	424
3e	504, 412	500, 414	414	412	416	414
3f	526, 422	528, 420	420	418	424	418
3g	518, 412	512, 412	410	410	416	408
3h	532, 404	518, 404	410	408	400	404
3i	522, 414	520, 414	414	410	420	414
3j	534, 422	524, 424	422	416	420	422
3k	524, 408	520, 410	412	414	414	410
3l	534, 391	532, 396	400	400	400	400
3m	530, 396	526, 398	402	400	400	404

recorded in Table 2. A sample ^{1}H NMR spectrum of dye 3c was given in Fig. 2.

According to Table 2, the peaks observed in the range of 14.06–14.31 ppm was amino (-NH_2) attached to the phenyl pyrazole ring, the peaks observed in the range of 13.42–13.99 ppm was amino (-NH_2) attached to the pyrazole ring, the peaks in the range of 12.67–12.84 ppm was imino (-NH) attached to the pyrazole ring and 11.73–12.03 the peaks in the ppm range were thought to belong to the hydroxyl (-OH) group attached to the phenyl pyrazole ring. In addition, the peaks seen in the range of 3.85–3.93 ppm belong to methoxy groups (**3c, 3g, 3k**) attached to the aromatic phenyl ring, and the peaks seen at 2.30–2.38 ppm to methyl groups (**3e, 3i, 3m**) attached to the aromatic phenyl ring.

As a result, the peaks of the hydroxyl group observed especially in the range of 11.73–12.03 showed that our compounds could be one of the tautomeric forms disazo-enol (**T1**) or hydrazo-azo-enol (**T6**) in DMSO solvent.

3.3. Solvent effect on UV-visible absorption spectra of dyes

UV-visible absorption spectra of dyes dissolved in 6 different solvents such as DMSO, DMF, acetonitrile, methanol, acetic acid and chloroform were measured over the wavelengths range (λ_{max}) between 350 nm and 700 nm in concentration 1×10^{-6} M. Analysis results are given in Table 3. Absorption spectrum of the dye 3m was showed in Fig. 3.

As seen in Table 3, two maximum absorption peaks were observed in DMSO and DMF solvents for all dyestuffs, while a single maximum absorption peak was observed in acetonitrile, methanol, acetic acid and chloroform.

An absorption peak of about 400 nm was seen in all solvents. Except for **3b** and **3d** compounds, there was no clear change in the maximum absorption bands for each of the solvents in this wavelength range for the other 11 dyes. It was observed hypsochromic shift in **3b** and **3d** dyes in acetic acid and methanol which are more acidic than other solvents. For these two dye compounds, the hypochromic shift seen in acetic acid and methanol indicates that these compounds transform into a different tautomeric structure in these solvents as given in Scheme 3.

In addition, a second absorption peak was observed around 500 nm in DMSO and DMF solvents, whereas this second peak was not observed in the other 4 solvents. This peak around 500 nm indicates that the dyestuffs may be ionized in these two solvents which have base properties compared to other solvents. As a result, this second absorption peak observed around 500 nm sug-

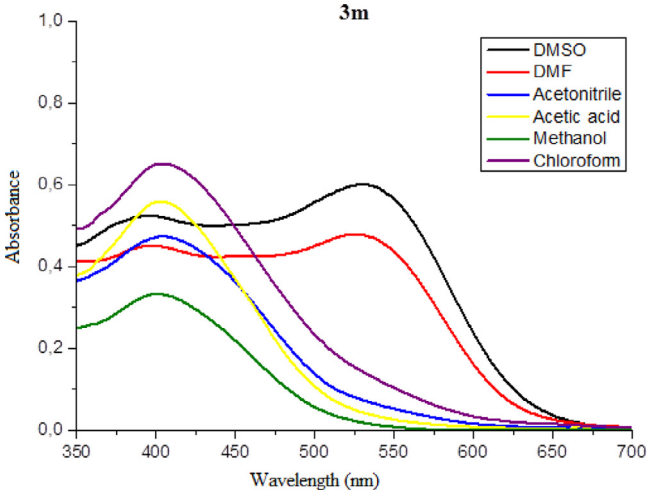


Fig. 3. Absorption spectra of dye **3m** in various solvents.

Table 4
Organic and inorganic acid-base effect on **3a-3m** dyes.

Dye No	Methanol	Methanol + HCl	Methanol + KOH	Chloroform	Acetic acid	Chloroform + Piperidine
3a	414	412	456	414	410	460
3b	366	366	478	426	362	462
3c	422	424	456	420	426	462
3d	366	364	476	424	362	450
3e	416	416	458	414	412	466
3f	424	422	464	418	418	446
3g	416	416	456	408	410	460
3h	400	406	456	404	408	462
3i	420	424	456	414	410	470
3j	420	426	490	422	416	518
3k	414	418	490	410	414	476
3l	400	406	482	400	400	502
3m	400	406	470	404	400	474

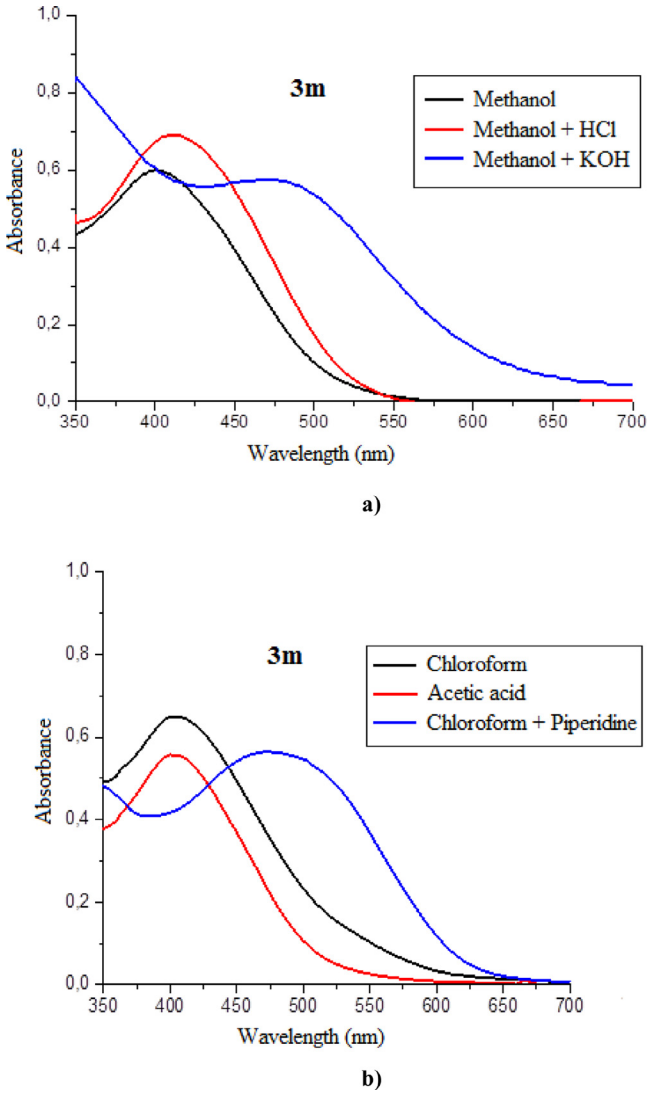


Fig. 4. Absorption spectra of dye **3m** in acidic and basic solutions; a) Inorganic acid-base, b) Organic acid-base.

gests that the dyestuffs dissolved in these two solvents transform into the anionic form shown in Scheme 3.

Considering all these data, while some of our synthesized dyestuffs showed hypsochromic shifts in acidic solvents, all of them formed a second peak at higher wavelength in basic solvents. This situation is a result we expect and target.

3.4. Organic and inorganic acid-base effect on UV-visible absorption spectra of dyes

Inorganic acid and base solutions were prepared by adding 0.1 M KOH and 0.1 M HCl into 10^{-6} molar methanol solvent of the dyes. The organic base solutions of the dyes were prepared by mixing equal amounts of methanol and piperidine solvents (1:1, v:v). The values measured on the instrument were reported in Table 4. The UV-visible spectrum of a sample dye (3m) measured in the presence of organic and inorganic acids and bases was given in Fig. 4.

All dyes gave a single absorption peak in acidic and basic solvents. These chemical shift values undergone bathochromic shift in the presence of inorganic bases. For example, all of the compounds showed bathochromic shift in alkaline methanol compared to methanol. There was no visible change in the λ_{max} values of the solvents obtained by adding acid in methanol according to methanol.

Likewise, with the addition of piperidine into chloroform, chemical shift values of dyes showed bathochromic shift compared to chloroform. There was no remarkable change in the UV-visible results of the dyes in acetic acid solvent compared to the chloroform solvent except for **3b** and **3d** Hypsochromic shifts were recorded in the absorption data of **3b** and **3d** dyes in acetic acid solvent. The common feature of these compounds is that both **3b** and **3d** dyes are bound to the para corner of the phenyl ring and have electron-withdrawing properties from the ring. This suggested that these two compounds transform into another tautomeric form in acetic acid solvent, as given in Scheme 3.

4. Conclusion

In this study, 13 new heterocyclic disazo dyestuffs were synthesized. The structures of the synthesized dyestuffs have been characterized using elemental analysis, infrared spectroscopy, nuclear magnetic resonance spectroscopy and mass spectroscopy methods. The effects of electron withdrawing and electron donating groups on the absorption ability of dyes in six different solvents were investigated. The synthesized dyes were found to have tautomeric properties and these tautomers were given in Scheme 3. The data obtained from the IR spectroscopy device were examined and it was seen that the dyes were in solid disazo-keto (T2) tautomeric form. According to the ^{1}H NMR data, the dyes could be in disazo-enol (T1) or (T6) tautomeric form, especially in DMSO solvent. In addition, all dyes showed a single maximum absorption peak in other solvents except DMSO and DMF, while two absorption peaks were observed in these two solvents. In addition, the second peak of these two solvents at around 500 nm showed that the dyes partially ionized in these two solvents.

Concequently, the synthesis of 13 new amino pyrazole derivative heterocyclic disazo dyestuff, which had many uses such as the textile, medicine, food, cosmetics, and dye industry, and whose popularity continues to increase day by day, was realized. With the synthesis of these new compounds, it was aimed dyestuffs have higher yield and brighter colors and to increase the variety of amino pyrazole derivative azo dyestuffs in the dye literature.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Aykut Demirçalı: Methodology, Conceptualization, Investigation, Data curation, Formal analysis, Writing - original draft.

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