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Synthesis, characterization and application of new azo dyes derived from uracil for polyester fibre dyeing

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ABSTRACT

Some novel uracil derived azo compounds were synthesized by diazotization of substituted aromatic amines, amidine- and guanidine-like amines such as 2-aminopyridine and 2-aminopyrimidine, ortho-hydroxy aniline and ortho-hydroxy naphthyl amines and coupling reaction with 6-amino-1,3-dimethyl-uracil. Structures of the dyes were fully characterized by spectroscopic techniques (UV, ^{1}H NMR, ^{13}C NMR, CHN and IR). The dyes were applied to polyester, affording orange-yellow shades and the wash fastness of the dyeings was excellent.

1. Introduction

Synthetic organic pigments are carbon based molecules manufactured by petroleum compounds, acids and other chemicals. In recent years, the fabrication of pyrimidine dyes has been intensively investigated, due to their unique industrial applications in hypnotic drugs [1], in living cells, in detecting cancer [2] and having pharmacological and biological activities [3–6]. Particularly uracil derivatives have aroused much interest owing to their potential applications in medicine and photobiology [7,8]. These compounds, typically pyrimidine-like structures, have an elegance role in heterocyclic chemistry [9]. Some derivatives of pyrimidine are prepared by use of 6-aminouracils as the starting material; for example, the reaction of 6-amino-1,3-dimethyluracil with an aldehyde and urea in the presence of an acid catalyst results in the formation of pyrimidopyrimides [10] or treating 6-amino-1,3-dialkyluracils with DMF–thionyl chloride in $CHCl_3$ at reflux, affords the 3-aminoisothiazolo [3,4-d] pyrimidine-4,6-diones that are useful as sedative, inflammation [11] and adenosine 3,5-cyclophosphate phosphodiesterase inhibitors [11,12]. As a third example, the reaction of these compounds with DMAD in refluxing methanol gives a pyrido [2,3-d] pyrimidine [13] of which, some of the oxo derivatives like 4-oxo-(NSC 112518) and 2,4-dioxopyrido [2,3-d] pyrimidine (NSC 112519) have antitumor activity against Walker muscular carcinosarcoma in rats [14]. Moreover, pyrido [2,3-d] pyrimidine-2,4-diones are prepared by the condensation of 6-amino-1,3-dimethyluracil with α,β-unsaturated carbonyl compounds [15].

Azo dyes are the most widely applicable in industry [16] with a world market share about 60–70% [17–19]. Some azo dyes were used in high technological systems, biological studies, plastics and polymers [20–28]. It can be expected that they make up the vast majority of the dyes discharged by textile-processing industries [29].

Among all, the long discussion on the structure of diazophenols has now been concluded. They feature the mesomeric structure (Scheme 1) and not a bezooxadiazole structure, but have structures that also called quininediazides, diazooxides and diazoquinones. These compounds have been widely studied in the literature [30–32] including their interesting photochemical properties [33–35]. Photolysis of diazotized *o*-aminonaphtholes has recently become important so-called photo-resist process in the production of semi-conductor elements. Furthermore, the diazotization of *o*-aminophenols and naphthols is important in the context of *o*,*o*′-dihydroxyazometal complex dyes [22].

Because of the mentioned importance of the uracil functional group, this paper is concerned with the synthesis and studying the structure of 6-amino-1,3-dimethyluracil azo component, the novel monoazo dyes based on the aryl and hetaryl systems (Scheme 2 and Table 1), as a possible replacement for methine and anthraquinone commercial dyes having similar color shades. In addition to synthesizing these new dyes, their unique application in dyeing polyester fibres and their spectroscopic properties were studied.

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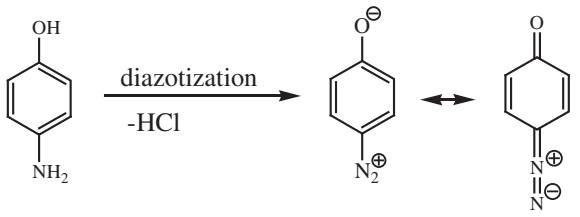


Scheme 1. Quinoid structure of para-hydroxyaryldiazonium salts.

2. Experimental

2.1. General remarks

All chemicals were purchased from Merck chemical company. The products were carefully isolated, purified and characterized by their spectroscopic data (UV, IR, ^{1}H NMR, ^{13}C NMR, CHN) and m.p. All yields refer to isolated products. ^{1}H NMR spectra of the dyes were recorded on a Bruker 500 spectrometer in either $CDCl_3$ or DMSO-d_6 as the solvent and TMS the internal standard. IR spectra were determined on a Perkin Elmer IR-1600. The electronic spectra and the elemental analysis were determined on a Hitachi U-2000 and a Vario-EL III CHN analyzer, respectively. TLC was carried out on plates coated with silica gel 60 F_{254}.

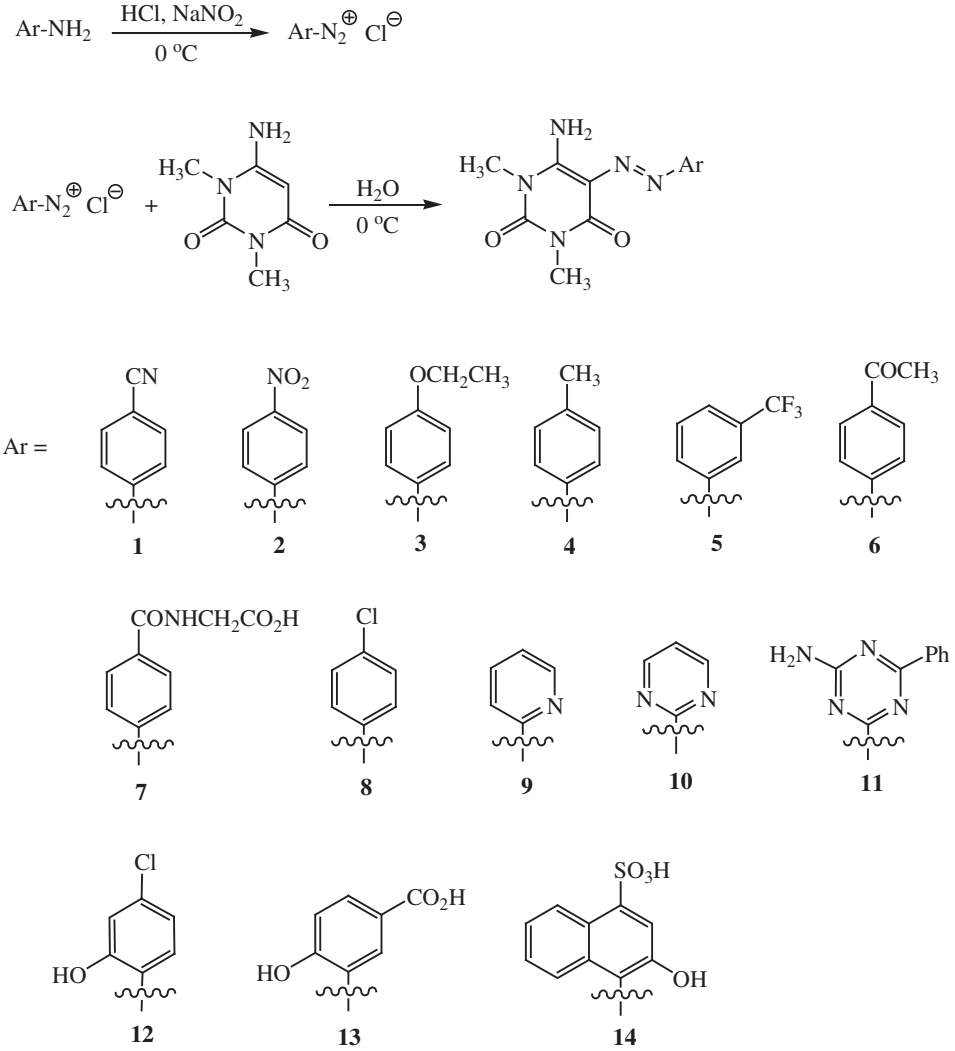
Table 1
Properties of the synthetic dyes.

Dye	M.p. (°C)	C%		H%		N%	
		Found	Calc.	Found	Calc.	Found	Calc.
1	270–273	54.47	54.93	4.12	4.25	29.37	29.56
2	316–318	47.42	47.37	3.79	3.98	27.47	27.62
3	234–236	55.38	55.44	5.51	5.65	22.93	23.09
4	262–263	57.04	57.13	5.44	5.53	25.57	25.63
5	324–326	47.56	47.71	3.59	3.70	21.46	21.40
6	284–286	55.65	55.81	4.89	5.02	23.17	23.24
7	303–305	50.22	50.00	4.53	4.48	23.36	23.32
8	259–261	48.98	49.07	4.17	4.12	23.79	23.84
9	257–260	50.84	50.77	4.73	4.65	32.23	32.29
10	234–236	55.38	55.44	5.51	5.65	22.93	23.09
11	262–263	57.04	57.13	5.44	5.53	25.57	25.63
12	324–326	47.56	47.71	3.59	3.70	21.46	21.40
13	284–286	55.65	55.81	4.89	5.02	23.17	23.24
14	303–305	50.22	50.00	4.53	4.48	23.36	23.32

2.2. Synthesis of the dyes

2.2.1. Method A

To an aqueous solution of the aromatic amine (2 mmol) and concentrated (12 M, 10 mmol) HCl placed in an ice bath (cooled to 0 °C) a cooled solution of sodium nitrite (2 mmol, 1.4 mL) was drop-wise added and the mixture vigorously stirred for 10 min.



Scheme 2. Some azo compounds synthesized from 6-amino-1,3-dimethyluracil.

2.1 mmol of 6-amino-1,3-dimethyluracil which dissolved in an aqueous NaOH (4 mmol, 1.6 mL) was added to this mixture and stirred for 30 min. After the HCl neutralizing and filtration, the product was crystallized from DMF.

2.2.2. Method B

A mixture of sodium nitrite (2 mmol) and concentrated H_2SO_4 (2 mL) at 0 °C was heated to 60 °C and again cooled to 0 °C. To this solution a (5:1 v/v) mixture of acetic and propanoic acids (3 mL) and aromatic amine (2 mmol) dissolved in (5:1 v/v) mixture of acetic and propanoic acids (2 mL) was added. After 2 h at 0 °C added the coupling agent (2 mmol) and the solution stirred for 6 h. The precipitated product was collected and purified by recrystallization from DMF.

2.2.3. Method C

$NaNO_2$ (70 mg, 1 mmol) was added to concentrated H_2SO_4 (1.0 mL) with external cooling. The suspension was heated to 60 °C and again cooled to 0–5 °C. To this cooled solution 0.2 mL of acetic acid was added and it was stirred for 10 min. The amidine-like and guanidine-like amine (1 mmol) dispersed in acetic acid (0.1 mL) was carefully added portion-wise and the mixture was stirred continuously for 2 h with external cooling (0 °C). To a cooled basic solution of 6-amino-1,3-dimethyluracil (1 mmol) in sodium hydroxide solution (2 mmol, 0.8 mL) the prepared diazonium solution was added drop-wise and the mixture was stirred for 20 min at reaction pH 7 (neutralized with sodium acetate). The precipitated product was filtered and purified by recrystallization from DMF.

Physical and spectroscopic data follow

6-Amino-1,3-dimethyl-5-(4-cyanophenyldiazenyl)uracil, (1): Yellowish solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.83 (br, 1H), 8.94 (br, 1H), 7.90 (d, 2H, J = 8.5 Hz), 7.80 (d, 2H, J = 8.5 Hz), 3.38 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 28.2 (CH_3), 29.2 (CH_3), 102.6 (C), 114.1 (C), 117.5 (CN), 122.2 (CH), 131.3 (CH), 151.2 (C), 157.4 (C=O), 161.7 (C=O), 178.2 (C).

6-Amino-1,3-dimethyl-5-(4-nitrophenyldiazenyl)uracil, (2): Orange solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 14.59 (br, 1H), 11.34 (br, 1H), 8.37 (dd, 2H, J = 7.2, 1.9 Hz), 7.72 (dd, 2H, J = 7.2, 1.9 Hz), 3.49 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 28.4 (CH_3), 29.3 (CH_3), 114.3 (C), 122.6 (CH), 127.5 (CH), 151.3 (C), 154.3 (C), 158.6 (C=O), 163.7 (C=O), 180.4 (C).

6-Amino-1,3-dimethyl-5-(4-ethoxyphenyldiazenyl)uracil, (3): Brownish crystal; ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.58 (br, 1H), 8.48 (br, 1H), 7.62 (d, 2H, J = 8.9 Hz), 7.01 (d, 2H, J = 8.9 Hz), 4.07 (q, 2H, J = 6.9 Hz), 3.62 (s, 3H), 3.24 (s, 3H), 1.39 (t, 3H, J = 6.9 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.9 (CH_3), 28.3 (CH_3), 29.1 (CH_3), 63.5 (CH_2), 112.4 (CH), 127.9 (CH), 144.6 (C), 153.0 (C=O), 152.5 (C), 157.0 (C=O), 176.3 (C).

6-Amino-1,3-dimethyl-5-(4-methylphenyldiazenyl)uracil, (4): Dark yellowish crystal; ^{1}H NMR (500 MHz, $CDCl_3$): δ 14.22 (br, 1H), 9.00 (br, 1H), 7.51–8.13 (m, 4H, ArH), 3.62 (s, 3H), 3.42 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.7 (CH_3), 28.4 (CH_3), 29.2 (CH_3), 113.6 (C), 122.7 (CH), 127.6 (CH), 138.5 (C), 147.9 (C), 154.5 (C=O), 160.1 (C=O), 178.2 (C).

6-Amino-1,3-dimethyl-5-(3-trifluorophenyldiazenyl)uracil, (5): Yellow crystals; ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.74 (br, 1H), 8.72 (br, 1H), 7.91 (s, 1H), 7.88 (d, 1H, J = 8.1 Hz), 7.58 (t, 1H, J = 8.1 Hz), 7.51 (d, 1H, J = 8.1 Hz), 3.42 (s, 3H), 3.29 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 29.3 (CH_3), 31.2 (CH_3), 115.0 (C), 124.8 (q, C, $^2J_{CF}$ = 11.0 Hz), 125.1 (CH), 126.0 (CH), 126.5 (CH), 127.8 (q, CF_3, $^1J_{CF}$ = 281.0 Hz), 153.0 (C), 156.6 (C=O), 162.2 (C=O), 178.0 (C).

6-Amino-1,3-dimethyl-5-(4-acetylphenyldiazenyl)uracil, (6): Yellow crystals; ^{1}H NMR (500 MHz, DMSO-d_6): δ 11,90 (br, 1H), 8.86 (br, 1H), 8.53 (dd, 2H, J = 6.9, 1.7 Hz), 7.76 (dd, 2H, J = 6.9, 1.7 Hz), 3.38 (s, 3H), 3.26 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.2 (CH_3), 28.8 (CH_3), 30.0 (CH_3), 114.0 (C), 122.8 (CH), 129.1 (CH), 137.5 (C), 152.1 (C), 153.1 (C=O), 157.9 (C=O), 177.1 (C), 196.3 (C=O).

6-Amino-1,3-dimethyl-5-(4-carboxyglycinophenyl diazenyl)uracil, (7): Light yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.86 (br, 1H), 8.80 (br, 1H), 8.13 (br, 1H), 7.92 (d, 2H, J = 8.4 Hz), 7.69 (d, 2H, J = 8.4 Hz), 3.76 (s, 3H), 3.40 (s, 3H), 2.91 (s, 1H), 2.76 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.3 (CH_3), 28.9 (CH_3), 38.8 (CH_2), 114.1 (C), 122.6 (C), 123.3 (CH), 128.2 (CH), 151.9 (C), 153.6 (C=O), 159.3 (C=O), 170.9 (C=O), 176.6 (C=O), 177.5 (C).

6-Amino-1,3-dimethyl-5-(4-chlorophenyldiazenyl)uracil, (8): Orange solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.24 (br, 1H), 9.43 (br, 1H), 7.58–8.34 (m, 4H, ArH), 3.66 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.4 (CH_3), 30.2 (CH_3), 117.6 (C), 123.8 (CH), 127.6 (CH), 128.8 (C), 149.9 (C), 156.7 (C=O), 162.6 (C=O), 179.4 (C).

6-Amino-1,3-dimethyl-5-(2-pyridodiazenyl)uracil, (9): Reddish crystals; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.92 (br, 1H), 9.02 (br, 1H), 8.59 (d, 1H, J = 5.4 Hz), 7.97 (d, 1H, J = 6.9 Hz), 7.10 (t, 1H, J = 6.9 Hz), 6.78 (t, 1H, J = 5.4 Hz), 3.23 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 28.2 (CH_3), 29.2 (CH_3), 117.5 (C), 119.5 (CH), 120.9 (CH), 136.1 (CH), 147.4 (CH), 153.5 (C=O), 158.4 (C=O), 171.6 (C), 177.8 (C).

6-Amino-1,3-dimethyl-5-(2-pyrimidodiazenyl)uracil, (10): Purple crystals; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.93 (br, 1H), 9.02 (br, 1H), 8.34 (d, 2H, J = 5.2 Hz), 6.43 (t, 1H, J = 5.2 Hz), 3.23 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 28.2 (CH_3), 29.2 (CH_3), 121.0 (C), 121.3 (CH), 152.7 (C=O), 156.2 (CH), 157.9 (C=O), 177.4 (C), 180.1 (C).

6-Amino-1,3-dimethyl-5-(4-amino-6-phenyltriazinediazenyl)uracil, (11): Violet crystals; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.91 (br, 1H), 9.03 (br, 1H), 8.16 (d, 2H, J = 7.5 Hz), 7.55 (t, 1H, J = 7.5 Hz), 7.48 (t, 1H, J = 7.5 Hz), 3.96 (br, 2H), 3.23 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 24.7 (CH_3), 29.0 (CH_3), 121.2 (C), 128.4 (CH), 132.5 (CH), 132.7 (CH), 132.8 (C), 153.3 (C=O), 158.3 (C=O), 168.4 (C), 172.1 (C), 178.5 (C), 192.7 (C).

6-Amino-1,3-dimethyl-5-(4-chloro-2-hydroxyphenyldiazenyl)uracil, (12): Yellowish crystals; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.11 (br, 1H), 11.04 (br, 1H), 8.80 (br, 1H), 7.75 (d, 1H, J = 2.6 Hz), 7.13 (dd, 1H, J = 8.7, 2.6 Hz), 6.88 (d, 1H, J = 8.7 Hz), 3.34 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 25.2 (CH_3), 28.8 (CH_3), 115.4 (CH), 124.2 (CH), 126.7 (CH), 129.3 (C), 133.9 (C), 148.1 (C), 153.4 (C=O), 160.7 (C=O), 178.0 (C).

6-Amino-1,3-dimethyl-5-(4-carboxylic-2-hydroxyphenyldiazenyl)uracil, (13): Yellowish crystals; ^{1}H NMR (500 MHz, DMSO-d_6): δ ^{1}H NMR (500 MHz, DMSO): δ 11.43 (br, 1H), 8.51 (br, 1H), 8.06 (d, 1H, J = 2.5 Hz), 7.91 (br, 1H), 7.83 (dd, 1H, J = 8.8, 2.5 Hz), 6.99 (d, 1H, J = 8.8 Hz), 3.33 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 24.2 (CH_3), 27.8 (CH_3), 113.6 (C), 114.4 (CH), 124.3 (CH), 124.8 (CH), 128.7 (C), 136.6 (C), 147.9 (C), 153.6 (C=O), 159.9 (C=O), 170.7 (C=O, carboxyl), 177.5 (C).

6-Amino-1,3-dimethyl-5-(2-hydroxy-4-sulfonicnaphthyldiazenyl)uracil, (14): Pink crystals; ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.33 (br, 1H), 8.67 (br, 1H), 8.13 (d, 1H, J = 2.6 Hz), 7.91 (br, 1H), 7.83 (dd, 1H, J = 8.5, 2.6 Hz), 7.07 (d, 1H, J = 8.5 Hz), 3.37 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 26.2 (CH_3), 28.9 (CH_3), 106.9 (CH), 114.2 (C), 119.3 (CH), 120.4 (CH), 129.8 (C), 130.7 (CH), 131.7 (C), 133.6 (C), 137.7 (C), 153.0 (C=O), 158.2 (C=O), 165.1 (C), 179.1 (C).

3. Results and discussion

Occasionally, aromatic amines having hydroxyl groups in *ortho* or *para*-position cannot be diazotized by straight forward nitrosation, due to an oxidation of the initial hydroxy amine. This occurs

with nitrosating reagents, forming the corresponding quinoid compounds. We suppressed the side reaction by performing the diazotization in the presence of copper or zinc salts.

Because of the strong basic properties, heteroaromatic amines especially amidine-like and guanidine-like ones are acid sensitive compounds and suppressed in acidic aqueous solutions before occurrence of any other process such as diazotization. In the best of our knowledge, there are a few reports about the convenient method to obtain azo dyes based on uracil, via coupling of a 6-amino-1,3-dialkyluracil with some diazonium salts. The use of a method containing a "naked nitrosonium ion" such as nitrosylsulfuric acid opens up new avenues for design of novel and amazing dyes. Based on previous studies we decided to prepare the new uracil based dyes that have high efficiency in industrial dyeing.

Firstly we synthesized the dyes by diazotization of the aromatic and heteroaromatic amines via the common method as "method A". The coupling reaction was performed in aqueous solution with 6-amino-1,3-dimethyluracil as the coupling component (Table 2). In eight cases (entries 1–8), the dyes were synthesized in moderate yields. The desired product obtained in low yield in the cases containing an electron donating groups (entries 3 and 4) on the ring. In the case of entry 1, IR spectra with distinctive signal at 2240 cm^{-1} and absence of any new carbonyl signal confirm that no hydrolysis to amide happened and cyano group remained intact. Especially, regarding the heteroaromatic amines (entries 9–11) and hydroxyaryl amines (entries 12–14), no noticeable product was observed. Rather, in these cases, fast suppressing of the amine occurred.

We tried to obtain these dyes by reducing the concentration of acid, but when this effected, no diazotization was observed.

Table 2
Synthesis of the new uracil azo dyes.

Dye number	Time (min)	Yield[a] (%)	Dye number	Time (min)	Yield[a] (%)
1	15	96	8	20	97
2	15	99	9	20	95
3	25	93	10	15	98
4	25	95	11	25	96
5	20	93	12[b]	20	96
6	15	96	13[b]	20	93
7	30	92	14[b]	20	94

[a] Based on method C: reaction conditions: sodium nitrite (1 mmol), concentrated H_2SO_4 (1.5 mL) was heated to 60 °C and again cooled to 0 °C, acetic acid (0.2 mL), aromatic amine (1 mmol) dissolved in acetic acid (0.1 mL), coupling agent (1 mmol) in sodium hydroxide solution (0.8 mL, 10% wt.); quenched after mentioned time.
[b] Performing the diazotization in the presence of zinc chloride (one equivalent for one equivalent of amine).

Previously, Towne et al. [36] reported a method for diazotization of amino-nitropyrazole and Gupta et al. [37] similarly introduced a method for diazotization of 5-amino-4-cyanopyrazoles by use of a mixture of acetic and propanoic acid (5:1 v/v). When we used a similar condition as "method B", we observed that the rates and yields of products 1–8 and 12–14 were decreased, and the dye **9** was obtained in low yield after 6 h. The reason for this effect is not clear at this time, however, it seems to conclude that the acid effect in this reaction depends mainly on three factors, namely, acidity, the softness of counter ion and the strongly nature of reagents.

To find the best condition in which all of yields raised and which is proper for the synthesis of heteroaromatic and hydroxyaryl amine-related dyes, we tested many acidic media. After these experiments we achieved a system, containing dilution of acidic media by 20% (v/v) acetic acid that improved all of yields. Using this procedure even in case of the amines with high-basic properties (entries 9–11), the diazonium ions were quantitatively prepared, trapped with 6-amino-1,3-dimethyluracil and then the prepared dyes were fully characterized by spectroscopic methods (Scheme 3). Also we prepared the dyes of *o*-hydroxy amines by this method and in the presence of 1 equivalent of zinc chloride in high yields (entries 12–14).

3.1. Dye uptake determination

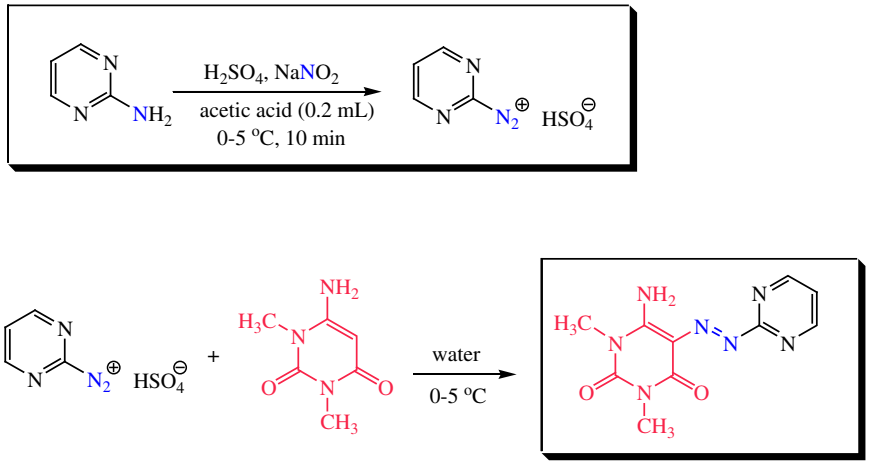
3.1.1. Standardized curve

To measure the dyes uptake, we determined λ_{max} values and extinction coefficients of dyes **1**–**7** according to the Beer Lambert law. For this reason dyes **1**–**7** (1.0×10^{-1} mmol) were dissolved in DMF (25 mL). Absorption of this solution (0.5 mL) was diluted to 10 mL with deionized water and allowed to stand overnight and then the absorption spectra were recorded (Fig. 1).

3.1.2. Uptake measurement

After the dissolution of the dyes (0.1 g) in water–DMF (19:1, 25 mL), the solution was sonicated. Dilution to 50 mL using deionized water–DMF (19:1) occurred and a portion of these dye solutions (0.1, 0.3, 0.5, 0.7, 0.9, 1.1, 1.3 mL) was placed in seven 25 mL volumetric flasks and the volume of each was adjusted to 25 mL using deionized water–DMF (19:1). Absorbance values were determined for each solution at λ_{max} as a function of dye concentration and linear standard curve for each dye was obtained.

To solutions prepared above in 50-mL flask, deionized water (10 mL) was added. A mechanical stirrer and a thermometer was placed in flask. At 25 °C, polyester fabric (1 g) was added and the time was recorded. Bath aliquots (1.0 mL) were removed and



Scheme 3. Synthesis of the guanidine-like dye.

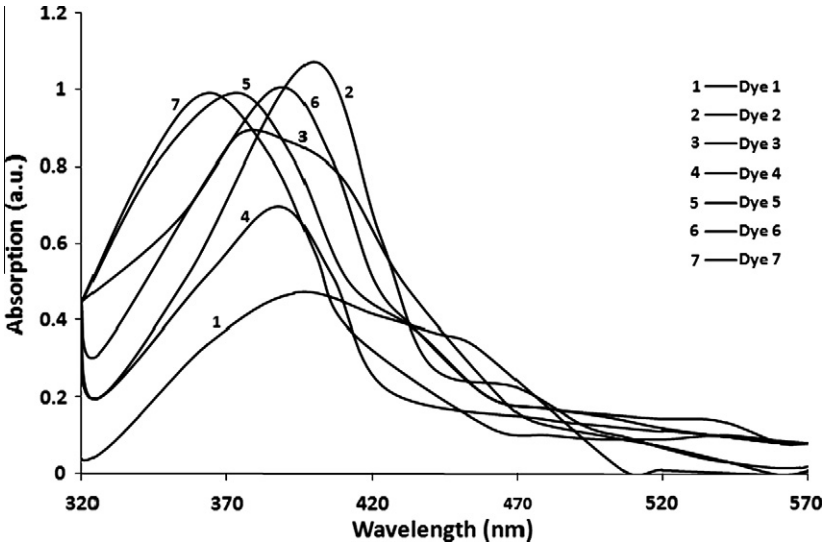


Fig. 1. Visible absorption spectra for dyes **1**–**7**.

diluted to 25 mL at the following times and temperatures: 5 min/25 °C, 8 min/35 °C, 15 min/40 °C, 30 min/60 °C, 50 min/90 °C, 70 min/95 °C, 100 min/95 °C, 120 min/95 °C, and 150 min/95 °C.

After the addition of 1 mL of DMF, the absorbance value of each solution was recorded at λ_{max} and the corresponding dye concentration was determined from the standard curve for the corresponding dye. The fabric quantities sufficient for fastness studies were obtained by repeating the dyeing process using 10 g of fabric samples (Fig. 2).

After treatments, the dyed fabric samples were washed with cold water and treated for 30 min at 50–60 °C with a solution containing fixing agent Y (5% omf) and aq. Acetic acid (2 mL), at a 30:1 liquor ratio. The dyed fabrics were washed, air-dried and ironed.

3.2. Fastness analysis

3.2.1. Light fastness

Light fastness assessment of dyed fabrics were done under irradiation in a commercial xenon arc weatherometer until the change in shade of blue-standard fabrics reached the 4–5 levels using the gray scale. The black panel temperature was 50 °C and the power of light was 1500 W. Light fastness values for dyes **1**–**7** were based on shade depth differences between unexposed and irradiated fabrics. As the result of hue and fastness properties of the dyes, polyester fabrics were dyed at 4% omf. The dyed fabrics were treated with 5% (w/w) cationic fixing agent (fixing agent Y). It was found that dyes **1**–**7** gave deep shades on polyester 4% omf (Table 3).

3.2.2. Wash fastness

For wash fastness assessment, dyed and after-treated fabric samples (50 × 30 mm) were attached to the same size undyed spun polyester fabric samples and immersed in a bath of 0.5% detergent at 35 °C and at a liquor ratio of 50:1.

After 30 min, the samples were removed, washed twice with deionized water, washed with tap water (four times), and air-dried below 50 °C. Changes in shade and staining of adjacent fabrics were evaluated with the aid of gray-scales for color change and transfer.

3.3. IR and NMR analysis of structures

Physical and spectral data of the dyes prepared are given in the experimental section. The dyes may exist in two tautomeric forms,

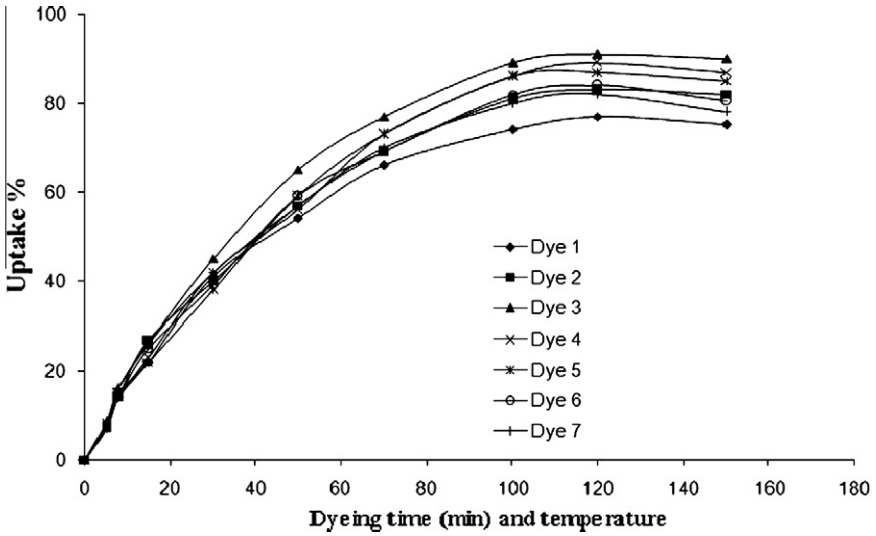
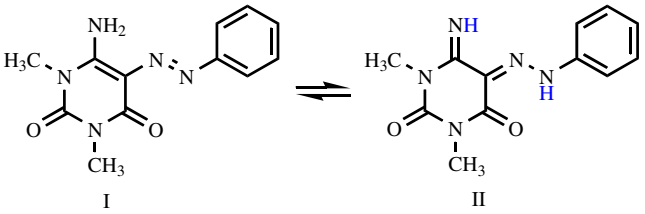


Fig. 2. Uptake of the dyes **1**–**7** on polyester fibre at 4% (omf).

Table 3
Shades and fastness properties for dyes **1–7** on polyester.

Dyes	Color	Wash fastness		Light fastness
		Change in shade	Staining on polyester	
1	Yellowish black	4	4–5	4
2	Orange	4	5	4
3	Dark yellow	3	3–4	3
4	Bright orange	4–5	4	3–4
5	Mustard yellow	4	4–5	3–4
6	Mustard yellow	4–5	5	4
7	Brick orange	3–4	4–5	3–4
8[a]	Yellow	3	4	2–3
9[b]	Yellow	3–4	4–5	2–3

[a] C. I. disperse yellow 31.
[b] C. I. disperse yellow 51.



Scheme 4. The tautomerism in the dyes.

as shown in Scheme 4. The infrared spectra of the dyes **1–14** in KBr) showed two strong bands within the range 3250 to 3550 cm^{-1}, due to —NH_2 band of the uracil ring [38,39]. The aromatic and aliphatic C—H stretching signals were recorded at 3000–3110 cm^{-1} and 2840–2980 cm^{-1}, respectively. Strong absorption bands appear at 1610 to 1700 cm^{-1} in the carbonyl region (Table 4). It can be suggested that these dyes exist as the azo-enamine form (**I**) in solid state.

The ^1H NMR spectra measured in DMSO-d_6 and $CDCl_3$ at room temperature showed broad singlet peaks at 11.58–14.59 ppm for one proton and at 8.48–11.34 ppm, that correspond to the tautomeric hydrazone NH and tautomeric imine NH respectively. It was reported that the hydrazone NH proton resonance appears approximately between 13.0 and 16.0 ppm, in ortho and para-hydroxyazo dyes [40,41]. These results show that all the dyes may exist predominantly as the hydrazone–imine form (**II**) in solution. Aromatic protons appeared at 6.88–8.59 ppm in doublet, triplet, doublet of doublet and multiplet forms owing to different H—H couplings. Other well-resolved and notable signals were singlets at 3.20–3.50 and 3.23–3.76 ppm for two different N—CH_3 groups on uracil section. For each compound the lower-field signal corresponds to the methyl group which lies between two carbonyl groups (3-position of the uracil) and the upper-field one corresponds to the other methyl.

3.4. UV–Vis absorption spectra

Solvent effect study of the dyes (Table 5 and Fig. 3) indicated that the increase in dipole moment of the solvent, increased λ_{max} of the dyes (bathochromic effect). Media of higher dipole moment stabilize the excited state more than the ground state and reduce the band gap between two levels. In the case of acetic acid, the pro-

Table 4
Characteristic IR absorption bands of uracil synthesized dyes.

Dye	νNH_2 (stretching) (cm^{-1})	$\nu C{=}O$ (stretching) (cm^{-1})	$\nu N{=}N$ (stretching) (cm^{-1})	Functional group (stretching) (cm^{-1})
1	3400, 3500	1640, 1700	1520	CN, 2240
2	3400, 3450	1635, 1680	1510	NO_2, 1340, 1520
3	3265, 3275	1620, 1695	1520	C—O, 1150
4	3245, 3260	1610, 1700	1520	C—H, 1360, 1450
5	3285, 3290	1615, 1700	1530	C—F, 1330
6	3260, 3300	1625, 1650	1520	C=O, 1700
7	3300, 3550	1650, 1690	1525	C=O, 1600
8	3300, 3550	1650, 1690	1525	C—Cl, 1170
9	3350, 3400	1650, 1700	1510	C=C, 1580, 1600
10	3350, 3400	1650, 1700	1515	C=C, 1570, 1580
11	3050–3400 (br)	1645, 1710	1520	C=N, 1575, 1610
12	Under overlap	1650, 1690	1510	O—H, 3100–3500 (br)
13	Under overlap	1660, 1700	1515	O—H, 2400–3550 (br)
14	3350, 3400	1665, 1710	1510	O—S=O, 1180, 1380

Table 5
UV–Vis absorption of dyes in various solvents, acidic and basic media.

Dye	λ_{max} in						ε_{max} (L mol cm^{-1})
	DMF (nm)	DMSO (nm)	Methanol (nm)	AcOH (nm)	MeOH/KOH (nm)	MeOH/HCl (nm)	
1	393	414	388	399	392	395	1.4×10^4
2	399	420	392	405	388	402	3.1×10^4
3	389	409	384	395	379	393	2.3×10^4
4	387	407	381	392	389	390	2.1×10^4
5	374	395	368	381	366	379	2.7×10^4
6	389	410	380	394	380	392	2.7×10^4
7	363	382	357	370	352	366	2.7×10^4
8	356	378	350	364	347	357	2.2×10^4
9	398	418	393	403	388	402	1.9×10^4
10	402	423	395	408	394	406	1.9×10^4
11	336	351	331	343	330	341	2.3×10^4
12	413	436	408	418	406	415	2.6×10^4
13	408	429	403	412	398	408	2.7×10^4
14	381	400	373	389	372	384	2.9×10^4

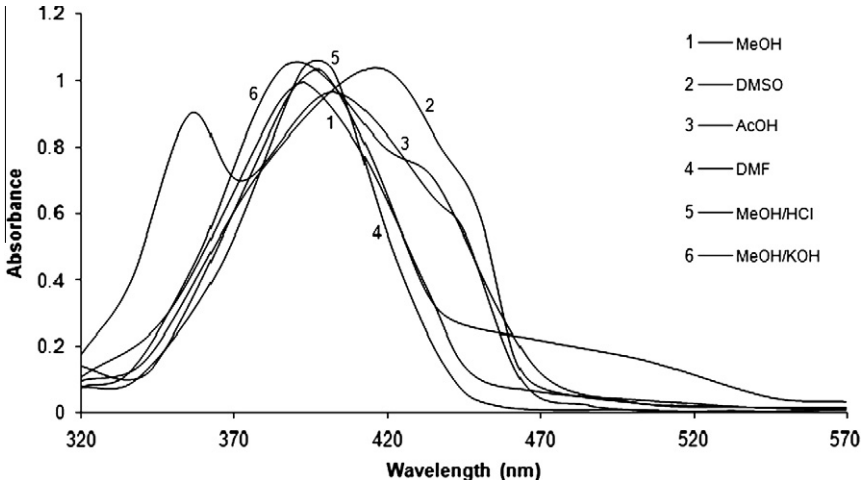


Fig. 3. Absorption spectra of dye **2** in various solvents.

tonation process caused the increase of the maximum absorption wavelength. The four solvents used in this test were DMSO, DMF, methanol and acetic acid with 46, 36, 32 and 6 Debye dipole moments, respectively.

Meanwhile, the effects of acidic and basic media on electronic spectrum of the dye **2** were recorded. Examination indicated that the acidic medium increases the mesomeric electron withdrawing effect of the nitro group by relative stabilization of its anionic form, and leads to increase of the λ_{max}. Conversely, basic medium decreases the λ_{max} value.

The observed λ_{max} is dependent on the nature of substituent. Mesomeric electron withdrawing groups (e.g. nitro and cyano) reduced the band gap by destabilization of the ground state. In contrast, the absorption band acquired a blue shift in presence of trifluoro as an inductive electron withdrawing group. This can be mainly attributed to the fact that it stabilized π and π^* orbitals, the latter to a lower degree. In the case of ethoxy, there were two contrasting features; inductive electron withdrawing and mesomeric donation, which caused this group not to have a detectable effect on maximum wavelength of absorption.

4. Conclusion

In summary fourteen dyes were prepared, in high yields, by diazotization of different aromatic, heteroaromatic and hydroxyaryl amines and coupling with 6-amino-1,3-dimethyluracil. The acid sensitive substrates were intact under these conditions. In the classical diazotization and even the nitrosylsulfuric acid methods no product was obtained for the amidine and guanidine-like amines. We synthesized the dyes derived from these amines in high yields using dilution of acidic medium with 20% (v/v) acetic acid. Structural effects of the uracil azo dyes on the color of polyester were studied. The dyeing afforded orange-yellow shades on polyester fabric, which are comparable color values to C. I. disperse yellow 31 and C. I. disperse yellow 51 (commercial dyes with high genotoxic features).

The results of fastness studies for the new dyes and related commercial dyes explained that the wash fastness properties of the dyes are excellent, with a rate around 4 for color change. Except dye **3**, all the other dyes gave very satisfactory results in the staining on polyester. The light fastness of all new dyes was quite acceptable and better in comparison with the commercial dyes. Eventually, dye **6**, providing good light fastness as well as little staining on polyester, was chosen as the best. Besides that, the new dyes do not contain the genotoxic methine and anthraquinone functionals. With regard to satisfactory wash fastness properties obtained from the dyeings, it is expected that if these new uracil dyes are less genotoxic than the corresponding commercial ones, they would be potential substitutes for those azo dyes. Study on genotoxicity of the new dyes is under way.

Appendix A. Supplementary material

Original ^{1}H NMR characterization data of the dyes, dyes IR spectra structural analysis, different schemes/figures in text and eyeful dyes in panorama. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.06.005.

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