

Light Fast Monoazo Dyes with an Inbuilt Photostabilizing Unit: Synthesis and Computational Studies

Rohit Bhide, Amol G. Jadhav, and Nagaiyan Sekar*

Tinctorial Chemistry Group, Department of Dyestuff Technology, Institute of Chemical Technology, Mumbai 400 019, India
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Abstract: A series of monoazo disperse dyes with a photostabilizing *o*-hydroxycarbonyl moiety was incorporated resulted in the enhancement of the light fastness properties on polyester and nylon substrates as compared to the dyes that do not possess the photostabilizing moiety. The geometries of the azo and the hydrazone tautomeric forms of all dyes were optimized at B3LYP/6-311+G(d) and electrophilicity index was calculated for propensity of the moiety to absorb electrons. The values of absorption and stability trend of the dyes were in good agreement with the trend of experimental light fastness values. These disperse dyes possess excellent wash fastness and moderate to good sublimation fastness on hydrophobic substrates.

Keywords: Monoazo disperse dyes, Light fastness, Fries rearrangement, Photo-physical properties, Electrophilicity index

Introduction

Accounting for over 50 % of all commercial colorants, the azo colorants, that have been studied more than any other class, are by far the most important class [1]. The relative ease in the synthesis of azo based colorants, the coverage of entire color gamut, and having an all-round applicability on textile [2,3], leather [4,5], polymeric substrates [6], and in non-traditional applications such as medical sciences [7] and liquid crystal displays [8] have made azo colorants the biggest shareholder in the production volume of colorants.

One of the impediments in the commercial triumph of an azo dye is its fastness to light. The change in hue or depth of color that is observed upon exposure of a dyed fiber to light depends on many factors such as the photostability of the dye, the dye concentration on the substrate, the wavelength distribution of the incident radiation, the nature of the fiber [9], and the composition of the atmosphere [10]. Profound research has been done and is still on-going to find out ways to enhance the lightfastness of azo dyes. Some of the reported methods include the introduction of carboxyl and sulfonate groups ortho to the azo group [11], aggregation of dye molecules on the surface of the substrate [12], the introduction of linear alkyl groups in the dye moiety having a chain length between C4-C8 [10], and post treatment with metal salts [13]. In case of disperse dyes, dyed polyester substrates show better lightfastness than dyed nylon substrates [14]. Some ways of improvement in the fastness to light include introduction of a nitro group meta to the azo group [15], an acetamide or an ester group ortho to the azo group [16-18], the introduction of N-cyanoethyl groups instead of N-hydroxyethyl groups [19], incorporation of fluorine [20] and silicon [21] in the dye moiety, and having a benzothiazole moiety with an electron withdrawing group at position 6

[22]. Some of the substituted thiazole monoazo disperse dyes have been extensively studied for their color-constitution relationship and fastness properties [23-25]. The use of UV absorbers in the dye formulation or as a post treatment to enhance the lightfastness of a dyed substrate is also extensively studied [26-32].

In this paper, we report the synthesis of novel monoazo disperse dyes by diazotizing different substituted primary aromatic amines and coupling with 2-hydroxy-5-methyl acetophenone. The solvent effect on absorbance characteristics of the synthesized azo dispersed dyes were studied in solvents of different polarities. These dyes were applied on polyester and nylon substrates and their fastness properties were measured. The monoazo disperse dyes containing acetyl group possess better photostability, as compared with the dyes which do not contain such an in-built photostabilizer. The probable reason may be generation resonance stabilized transient tautomers of keto-enol along with aza-hydrazone mechanism of the molecule [33].

Experimental

Materials and Characterization

p-Cresol, acetic anhydride, aluminium chloride, aniline, *p*-chloro aniline, *p*-amino benzonitrile, *p*-nitro aniline, 2-cyano-4-nitro aniline, sodium nitrite, sodium hydroxide, Metamol (dispersing agent), conc. H₂SO₄, and conc. HCl were purchased from S. D. Fine Chemicals Ltd., Mumbai, India. All reagents were characterized by melting or boiling point and used without further purification. Solvents were used after distillation at their boiling point and drying according to standard processes.

All the synthesized dyes were purified by recrystallization and their melting points were recorded on an instrument from Sunder Industrial Product, Mumbai. Spectronic Genesys 2 UV-visible spectrophotometer and Jasco 4100 Fourier

*Corresponding author: n.sekar@ictmumbai.edu.in

Transform IR instrument were used to record the absorption spectra and IR spectra of the synthesized dyes. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on an Agilent NMR VNMRS spectrometer at a ^1H frequency of 500 MHz and a ^{13}C frequency of 150 MHz, respectively. The chemical shift values are expressed in δ ppm using CDCl_3 as a solvent and TMS as an internal standard. Mass spectra were recorded on a Finnegan Mass spectrometer. DFT calculations were performed on a HP workstation XW 8600 with Xeon processor, 4GB RAM, and Windows Vista as operating system. The software package used was Gaussian 09W. The ground state geometry was optimized at B3LYP level of theory and 6-311G (d) as basis set.

Synthesis and Identification

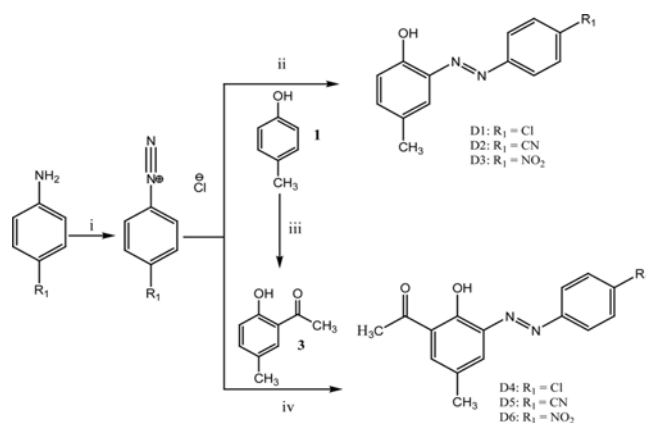
The synthetic scheme for the preparation of dyes **D1-D6** is shown in Scheme 1. 2-hydroxy-5-methyl acetophenone (**3**) was prepared by the reported procedure from *p*-cresol acetate (**2**) via Fries rearrangement (Scheme 1) [34].

Preparation of Azo Dyes D1 ((E)-2-(2-(4-chlorophenyl) diazenyl)-4-methylphenol), D2 ((E)-2-(2-(4-cyanophenyl) diazenyl)-4-methylphenol), and D3 ((E)-2-(2-(4-nitrophenyl) diazenyl)-4-methylphenol)

These dyes are reported in literature [35-37] and were prepared by known procedure [38]. The percentage practical yield, melting points and FT-IR values are tabulated (Table S1-Supporting Information).

Preparation of Azo Dyes (D4-D6)

The solution containing amine (0.0033 mol), conc. HCl (3 ml, 0.035 mol), and water (25 ml, 1.388 mol) was boiled till a clear solution was obtained. This solution was then gradually cooled to 0°C . The acidity of the solution was checked by means of Congo red paper. Sodium nitrite (0.25 g, 0.0036 mol) was then gradually added with stirring to the above solution maintaining the temperature of the



Reaction conditions: (i) conc. HCl, NaNO_2 , $0-5^\circ\text{C}$; (ii) *p*-cresol, NaOH, Na_2CO_3 , $0-5^\circ\text{C}$; (iii) Ac_2O , NaOH, $0-5^\circ\text{C}$ and AlCl_3 , 130°C , 90 min; (iv) 2-hydroxy-5-methyl acetophenone, NaOH, Na_2CO_3 , $0-5^\circ\text{C}$

Scheme 1. Synthesis of mono azo disperse dyes (**D1-D6**).

solution below 5°C . Starch iodide paper was used as a process control test. After complete addition, the solution was further allowed to be stirred for 20 min at 5°C . Urea was added to destroy the excess nitrous acid. Meanwhile, the coupler solution containing 2-hydroxy-5-methyl acetophenone (0.5 g, 0.0033 mol), sodium hydroxide (0.16 g, 0.004 mol), sodium carbonate (1.06 g, 0.01 mol), and 50 ml water was cooled to 0°C . With continuous stirring, the diazonium salt solution was gradually added to the coupler solution maintaining the temperature below 5°C . After complete addition is done, the mixture is further stirred for 3 h. The precipitated crude dye is then filtered using a nutsche and further recrystallized using 75 % methanol solution and finally dried.

D4: 1-((E)-3-(2-(4-chlorophenyl) diazenyl)-2-hydroxy-5-methylphenyl)ethanone

Yield: 95 %, Melting point: $132-134^\circ\text{C}$

HRMS (FAB+) m/z : calcd for $[\text{M}+\text{H}]^+$, 289.0744; found, 289.0744

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): 2.39 (s, 3H, Ar-CH₃), 2.71 (s, 3H, CO-CH₃), 7.45 (s, 2H, Ar-H), 7.76 (s, 1H, Ar-H), 7.80 (s, 1H, Ar-H), 7.88 (s, 2H, Ar-H), 13.20 (s, 1H, -OH)

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): 20.41, 28.98, 76.76, 77.01, 77.27, 123.69, 123.97, 128.34, 129.50, 130.63, 137.25, 139.82, 150.16, 155.69, 202.09

FT-IR: 2980, 1644, 1437, 1115 cm^{-1}

D5: 1-((E)-3-(2-(4-cyanophenyl) diazenyl)-2-hydroxy-5-methylphenyl)ethanone

Yield: 84 %, Melting point: $150-154^\circ\text{C}$

HRMS (FAB+) m/z : calcd for $[\text{M}+\text{H}]^+$, 280.1086; found, 280.1052

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): 2.40 (s, 3H, Ar-CH₃), 2.71 (s, 3H, CO-CH₃), 7.82 (s, 4H, Ar-H), 7.98 (s, 2H, Ar-H), 13.18 (s, 1H, -OH)

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): 20.44, 28.41, 76.76, 77.01, 77.27, 114.09, 118.36, 118.69, 123.29, 128.41, 133.30, 133.60, 135.60, 140.27, 154.06, 202.71

FT-IR: 3064, 2227, 1648, 1441, 1115 cm^{-1}

D6: 1-((E)-3-(2-(4-nitrophenyl) diazenyl)-2-hydroxy-5-methylphenyl)ethanone

Yield: 80 %, Melting point: $176-180^\circ\text{C}$

HRMS (FAB+) m/z : calcd for $[\text{M}+\text{H}]^+$, 300.0984; found, 300.0945

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): 2.40 (s, 3H, Ar-CH₃), 2.71 (s, 3H, CO-CH₃), 7.80 (d, $J = 12.5\text{Hz}$, 1H, Ar-H), 8.02 (s, 2H, Ar-H), 8.36 (s, 3H, Ar-H), 13.17 (s, 1H, -OH)

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): 20.44, 28.33, 76.77, 77.02, 77.28, 123.10, 123.86, 124.35, 125.41, 128.45, 135.84, 140.39, 148.70, 155.29, 202.71

FT-IR: 3105, 1645, 1517, 1341, 1105 cm^{-1}

General Procedure of Dyeing

Disperse dyeing of polyester and nylon fabric was carried out using high temperature high pressure method in a Rossari Labtech Flexi Dyer dyeing machine with a material

to liquor ratio of 1:20. 2 % Dye was used for fabric dyeing (calculated on weight of the fabric). All synthesized azo disperse dyes have very less solubility in water. Firstly dye was dissolved in 5 ml of N,N-dimethylformamide and diluted with 15 ml of buffered solution of pH 5 made by using sodium acetate and acetic acid in water. Fine dispersion of the dye in water was obtained after ultrasonication for 15 min. Metamol was used as a dispersant. Polyester fabric and nylon were dyed using the above solution. Dyeing was commenced at room temperature. The dye bath temperature was raised at a rate of 3 °C min⁻¹ to 130 °C and 80 °C, respectively, maintained at this temperature for 60 min, and rapidly cooled to 50 °C. The dyed fabrics were rinsed under cold water and then reduction cleared in an aqueous solution of 1 g/l sodium hydrosulfite and 1 g/l sodium hydroxide using 1:50 liquor to goods ratio at 80 °C for 30 min. The treated fabrics were rinsed by cold water and allowed to dry in the open air.

Results and Discussion

Preparation of Azo Dyes

The dyes, in which *p*-cresol was used as a coupler, gave better yields than the dyes in which 2-hydroxy-5-methyl acetophenone was used as a coupler, owing to the deactivation of the latter because of the electron withdrawing acetyl group. Also, the rate of reaction was much faster in case of *p*-cresol based azo dyes. Typically, the coupling reaction in case of *p*-cresol took a maximum of 30 min, whereas, in case of 2-hydroxy-5-methyl acetophenone, it took a minimum of 3 h. It was observed that a chloro group at para position to the diazonium group gave the best yields of the series (Yields D1=92 %, D4=95 %), which can be attributed to the

stability of the diazonium salt because of the chloro group.

For weakly basic primary aromatic amines, containing 2 electron withdrawing groups, the nitrosyl sulfuric acid diazotization method was employed. This method resulted in lower yields than the direct diazotization method because of the stability issues of the highly reactive diazonium salts.

Photo-physical Properties

20 μM solutions of the dyes were made using 8 different solvents, viz. DCM, chloroform, ethyl acetate, dioxane, methanol, acetonitrile, DMF, and DMSO. The UV-Vis spectra of the azo dyes were recorded on a Perkin Elmer UV-Vis spectrometer Lambda 25. All the azo dyes show a broad and a dual absorption with different absorbance values. Also these dyes do not show any significant solvatochromism. The effect of substituents on the wavelength of maximum absorption was as expected, i.e. electron donors showing a hypsochromic shift, whereas electron withdrawing groups showing a bathochromic shift in the order: -Cl < -CN < -NO₂ (Table 1).

The presence of an acetyl group in the coupler moiety brought about a hypsochromic effect with the dyes **D1-D3** having a longer wavelength of maximum absorption than the dyes **D4-D6** (Figure 1).

Polyester and Nylon Dyeing

The synthesized disperse dyes were applied on polyester and nylon fabrics using high temperature high pressure method in a Rossari Labtech Flexi Dyer machine. 5 % shade was used for dyeing and the material:liquor ratio was kept 1:40. 2 g/l dispersing agent (Metamol) and levelling agent was added to the dye bath to achieve level dyeing. The pH of the dye bath was kept 4.5-5.0 by adding dilute acetic acid.

Table 1. λ_{max} of dyes in various solvents

Dye	DCM		CHCl ₃		Ethyl acetate		Dioxane		MeOH		ACN		DMF		DMSO	
	λ _{max} (nm)	ε (dm ³ mol ⁻¹ cm ⁻¹)	λ _{max} (nm)	ε (dm ³ mol ⁻¹ cm ⁻¹)	λ _{max} (nm)	ε (dm ³ mol ⁻¹ cm ⁻¹)	λ _{max} (nm)	ε (dm ³ mol ⁻¹ cm ⁻¹)	λ _{max} (nm)	ε (dm ³ mol ⁻¹ cm ⁻¹)	λ _{max} (nm)	ε (dm ³ mol ⁻¹ cm ⁻¹)	λ _{max} (nm)	ε (dm ³ mol ⁻¹ cm ⁻¹)	λ _{max} (nm)	ε (dm ³ mol ⁻¹ cm ⁻¹)
D1	332	114000	333	94000	331	120000	332	194000	330	96000	329	102000	333	96000	330	90000
	399	46000	400	36000	398	52000	398	86000	396	38000	395	40000	394	52000	395	56000
D2	333	60000	335	36000	333	62000	332	108000	331	52000	328	52000	334	48000	334	40000
	418	22000	421	7400	411	24000	411	44000	407	18000	409	18000	409	24000	409	22000
D3	342	172000	342	190000	338	152000	339	140000	339	120000	337	200000	342	118000	343	104000
	424	64000	428	68000	418	58000	417	56000	412	66000	415	100000	415	72000	417	76000
D4	330	140000	331	110000	325	110000	333	100000	327	102000	325	104000	330	132000	329	104000
	392	118000	392	88000	390	96000	392	84000	388	86000	387	86000	392	116000	392	92000
D5	330	124000	330	116000	325	110000	328	98000	327	128000	327	114000	330	120000	331	124000
	395	102000	397	90000	394	100000	395	82000	392	104000	391	96000	396	102000	398	110000
D6	334	134000	331	178000	330	130000	332	118000	328	74000	330	132000	333	120000	333	114000
	401	122000	401	124000	400	120000	399	108000	398	68000	398	122000	405	110000	407	110000

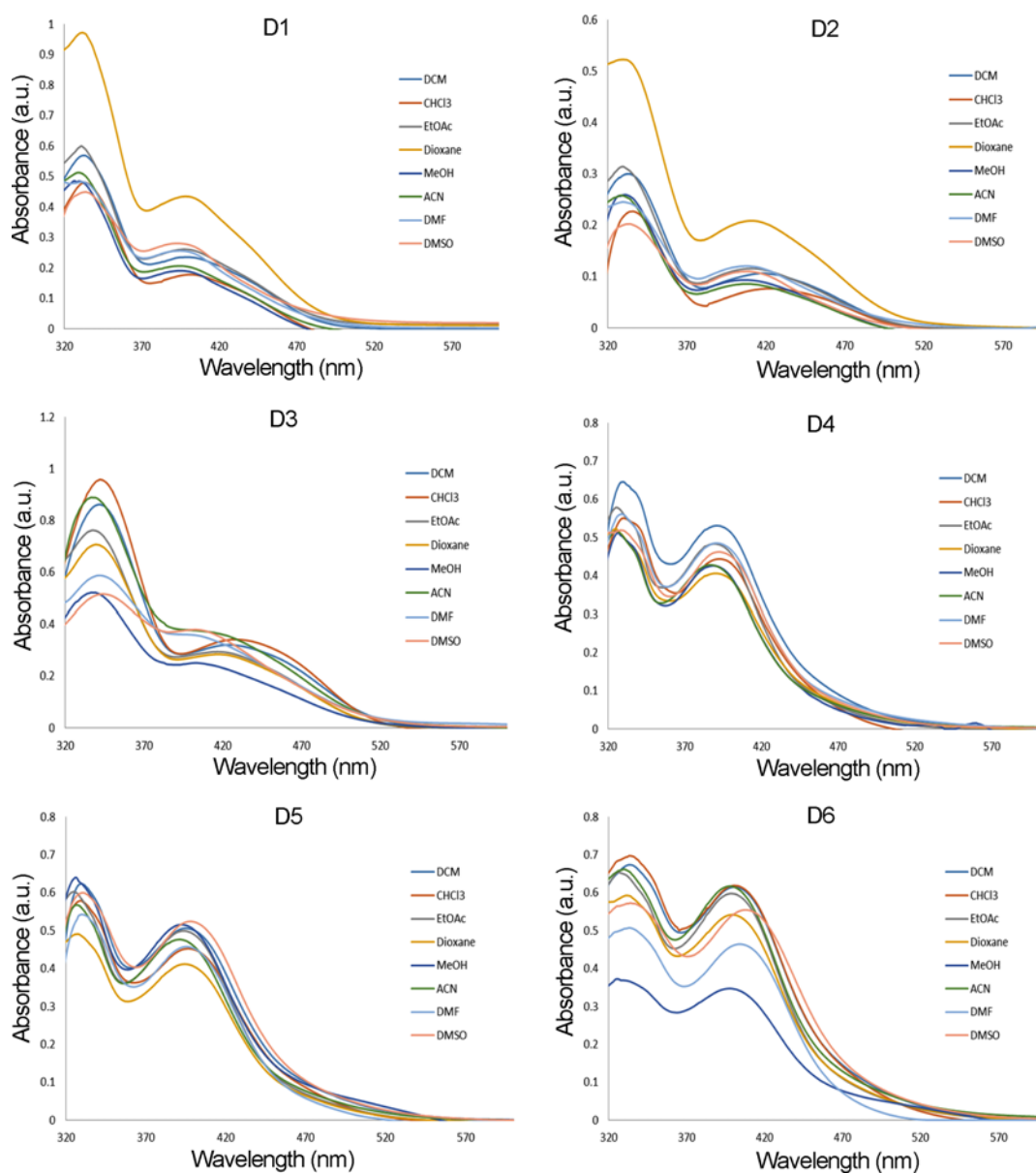


Figure 1. Absorption spectra of dyes in different solvents (Note: D1, D2, D3, D4, D5, and D6 are the absorbance graphs of corresponding dyes).

The rate of heating was 2 °C/min and the temperature was maintained at 130 °C for 1 h. After cooling, the dyed samples were washed first with cold water and then with hot water, followed by reduction clearing in 2 g/l solution of sodium hydrosulfite and sodium hydroxide at 70 °C for 20 min. The samples were then rinsed with cold water and finally dried.

Color Assessment

The K/S and L^* , a^* , b^* values of the dyed samples were measured using a Spectrascan 5100+ instrument. Dyed polyester samples showed better levelling than the dyed nylon samples. Also the color looked brighter on polyester

than on nylon. The K/S values were higher for nylon, than that for polyester (Table 2 and 3).

Fastness Properties

Light Fastness

The light fastness of the dyed samples was measured in which half part of the sample was exposed to a xenon lamp for 17 hours while the other half was covered. The samples were then compared with the Blue wool standard scale and fastness ratings were given. The K/S and dE values of the dyed samples were measured after exposure using the Spectrascan 5100+ instrument.

The dyes with an acetyl group on the coupler (D4-D6) had

Table 2. Color coordinates (CIELAB) for polyester dyeing

Dye	L^*	a^*	b^*	c^*	h^0	K/S
D1	65.818	22.214	73.974	77.237	73.256	19.6650
D2	60.062	31.071	71.003	77.504	66.339	20.8070
D3	57.113	33.399	66.705	74.599	63.377	20.3060
D4	60.236	22.801	66.937	70.714	71.161	20.2072
D5	53.747	31.455	59.651	67.436	62.172	20.2072
D6	53.097	26.754	56.019	62.080	64.445	19.5124

Table 3. Color coordinates (CIELAB) for nylon dyeing

Dye	L^*	a^*	b^*	c^*	h^0	K/S
D1	59.829	17.151	57.973	60.457	73.490	16.5643
D2	62.755	20.728	67.463	70.576	72.891	17.5046
D3	51.025	30.439	61.975	69.047	63.816	27.8770
D4	48.951	27.032	47.498	54.652	60.331	24.8095
D5	44.031	22.081	34.685	41.117	57.495	16.442
D6	30.679	21.261	30.646	37.299	55.226	29.7018

Table 4. Light, wash and sublimation fastness ratings for dyed polyester and nylon samples

Dye	Polyester			Nylon		
	Light fastness rating (1-8)*	Wash fastness rating (1-5)*	Sublimation fastness rating (1-5)*	Light fastness rating (1-8)*	Wash fastness rating (1-5)*	Sublimation fastness rating (1-5)*
D1	6	3	3	4-5	3	3-4
D2	6	3	3	4-5	3	3
D3	6-7	3-4	3	5	3-4	3
D4	6-7	4	3	5	4	3-4
D5	6-7	4	3	5	4	3-4
D6	6-7	4	3	5	4	3-4

Rating* (Light fastness: 1-poor and 8-Excellent) (Wash Fastness: 1-poor and 5-Excellent) (Sublimation Fastness: 1-poor and 5-Excellent).

approximately half a scale better light fastness than the dyes without an acetyl group (Table 4). Also the dE values were less for the dyes with acetyl group than the dyes without an acetyl group. The lowest % change in K/S , in case of dyed polyester samples, was for **D4** (0.67 %) and the highest % change was showed by **D1**, whereas in case of dyed nylon samples, the lowest and the highest % change in K/S was showed by dyes **D3** and **D6**, respectively. The fastness rating for dyed polyester samples was approximately one and a half scale more than that for dyed nylon samples, i.e. good to excellent rating for polyester, whereas, fair to good for nylon.

Wash Fastness

The dyed samples were rated for wash fastness. The standard test was used in which the dyed sample was sandwiched between two different undyed cloth samples (cotton and polyester/nylon) and then treated with 5 g/l soap solution for 30 min at 70 °C. Two parameters, i.e. color

change (cc) and color staining (on undyed cloth) [cs] were rated by comparing with standard scale after wash treatment.

The wash fastness in case of polyester samples was excellent, whereas it ranged from moderate to excellent, in case of dyed nylon samples (Table 4).

Sublimation Fastness

The dyed samples were sandwiched between two undyed cloth pieces (cotton and polyester/nylon) and were subjected to 180 °C for 30 s in a sublimation fastness tester. Two parameters, i.e. color change (cc) and color staining (on undyed cloth) [cs] were rated.

Sublimation fastness ranged from moderate to good (Table 4). Also it was half scale better in case of polyester than the dyed nylon samples.

Electrophilicity Index

As a verification for the experimentally deduced light

fastness properties, it was decided to calculate the photostability of the dyes mathematically. For this reason, the electrophilicity index (ω) was utilized. As defined by Parr *et al.* [39,40], this electrophilicity index measures the propensity of the moiety to absorb electrons and is mathematically formulated as:

$$\omega = \frac{\mu^2}{\eta}$$

where ω =electrophilicity index, μ =chemical potential, and η =chemical hardness

The chemical potential and the chemical hardness for a molecule can be determined using the following equations:

$$\mu = -\frac{(IP+EA)}{2}$$

$$\eta = \frac{(IP-EA)}{2}$$

where IP =ionization potential, i.e., the change in the energy when an electron is removed from the system and EA =electron affinity, i.e., the change in the energy when an electron is added to the system.

But to obtain IP and EA , one must find out the three energy values, i.e. E_N , E_{N+1} and E_{N-1} , where E is the total energy of the system and N is the number of electrons, which makes the whole process tedious and time consuming.

So, in order to save time, one can find out the values of chemical potential and hardness by using Koopmans' theorem:

$$\mu = \frac{(E_{LUMO} + E_{HOMO})}{2}$$

$$\eta = \frac{(E_{LUMO} - E_{HOMO})}{2}$$

where, E_{LUMO} is the energy of the lowest unoccupied molecular orbital and E_{HOMO} is the energy of the highest occupied molecular orbital.

Also, net electrophilicity can be defined as:

$$\omega^\pm = \omega^+ + \omega^-$$

$$\text{where } \omega^+ = \frac{(E_{LUMO})^2}{2(E_{LUMO} - E_{HOMO})} \text{ and } \omega^- = \frac{(E_{HOMO})^2}{2(E_{LUMO} - E_{HOMO})}$$

The geometries of the azo and the hydrazone tautomeric forms (Figure 2) of all dyes were optimized at B3LYP/6-311G(d) level of theory. Gaussian 09 program package was used for this geometric optimization. The values of E_{LUMO} , E_{HOMO} , total energy (E), and dipole moment were extracted from the Gaussian output files.

From Table S2 (Supporting Information), it can be seen that the value of total energy (E) for hydrazone form of all the dyes is less than the azo form, which concludes that the hydrazone form is more stable than the azo, and the dyes exist in the hydrazone form and not the azo in the gas phase.

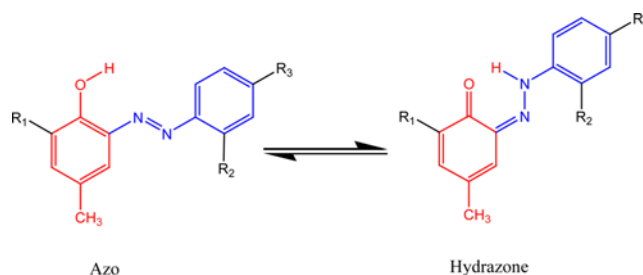


Figure 2. General tautomeric forms of the synthesized monoazo disperse dyes.

The HOMO and LUMO energies, chemical potential (μ), and chemical hardness (η) decrease from **D1** to **D3** and from **D4** to **D6**.

The value of electrophilicity index (ω) for dyes containing acetyl group in hydrazone form is more than value of ω for dyes without an acetyl group in the hydrazone form. But in case of the azo form, the value of ω for dyes containing acetyl group is less than value of ω for dyes without an acetyl group. But as the hydrazone form is more stable than the azo form, the value of ω of the hydrazone form determines the photostability of the dyes. The electrophilicity index measures the energy stabilization, when an optimal electronic charge transfer from the environment to the system occurs. Hence, when electron is transferred to the molecule, the molecule is stabilized more if the value of ω is more, and therefore such molecules exhibit higher light fastness.

The same correlation is valid for the net electrophilicity values; i.e. higher the value of ω^\pm , more will be the light fastness. From Table S2 (Supporting Information), it is again very clear that the dyes containing an acetyl group have a higher value of net electrophilicity than the dyes without an acetyl group.

Also, larger the ω^+ value corresponds to a better capability of accepting charge and smaller value of ω^- makes the molecule a better electron donor. From Table S2 (Supporting Information), one can observe higher ω^- for dyes with an acetyl group than the dyes without an acetyl group, hence the dyes without an acetyl group are better donors and dyes with an acetyl group are better electron acceptors.

Optimized Geometries of Dyes

Ground state geometries of the all dyes were optimized at B3LYP/6-311+G(d) levels. Optimized bond lengths of the synthesized dyes in different solvents are tabulated in Table S3a-h (Supporting Information) respectively. Figure S1 (Supporting Information) shows optimized geometries of azo and hydrazone tautomers of D1 in chloroform. The computed $N_{16}-N_{17}$ (D1A) bond lengths increased from 1.25724 Å to 1.26556 Å $N_{15}-N_{16}$ (D1H) also O-H bond lengths increased from 0.97301 Å (D1A) to 0.98966 Å (D1H) and N-H bond lengths decreased from 3.3482 Å (D1A) and 1.75505 Å (D1H). Similar trend was observed

with all the dyes in all the solvents showing clear azo-hydrazone tautomerism (Figure S1 and Table S3a-h (Supporting Information)).

The N=N bond lengths of azo form (D1A, D2A, D3A, D4A, D5A, and D6A) was increased in hydrazone form (D1H, D2H, D3H, D4H, D5H, and D6H) due to the hydrogen bonding. From the computational data (calculated energies ($E/\text{hartree}$), Gibbs free energies ($\Delta G/\text{hartree}$), relative energies ($\Delta E/\text{kJ}\cdot\text{mol}^{-1}$), and Interatomic distance it is observed that compounds exit predominantly in hydrazone form (Table S3 a-h, Table S4 a-h).

Calculated Energies of Azo-Hydrazone Tautomeric Forms

To find out stability of azo and azo-hydrazone forms calculated energies ($E/\text{hartree}$), Gibbs free energies ($\Delta G/\text{hartree}$), and relative energies ($\Delta E/\text{kJ}\cdot\text{mol}^{-1}$) of the chromophores of the synthesized dyes in their azo and hydrazone tautomeric forms were calculated at B3LYP/6-311+G(d) level in different solvents (Table S4 a-h: Supporting Information). It is clear that the hydrazone form of without acetylated compounds (D1H, D2H, and D3H) are more stable than the corresponding azo form (D1A, D2A, and D3A) by 6.91-17.32 $\text{kJ}\cdot\text{mol}^{-1}$ while reverse is the case with acetylated compounds D4, D5, and D6 in all the solvents (Table S4 a-h). In gas phase hydrazone forms of all the compounds are more stable than azo forms (Table S4 i) [41].

Electronic Vertical Excitation Spectra (TD-DFT)

Electronic vertical excitations were calculated using TD-

B3LYP/6-311+G(d) method in gas phase as well as in chloroform, dichloromethane, ethyl acetate, dioxane, methanol, acetonitrile, N,N-dimethylformamide, dimethyl sulfoxide solvents of different polarities. Experimental absorbance spectra, computed vertical excitation spectra associated with their oscillator strength (f), orbital contribution, and percentage deviation of the dyes in chloroform and other solvents are shown in Tables 5 and Tables S5 a-g (Supporting Information), respectively.

HOMO-LUMO Comparison

The comparative increase and decrease in the energy of the occupied (HOMOs) and virtual orbitals (LUMOs) gives a qualitative idea of the excitation properties and the ability of hole or electron injection [32]. The HOMO (azo form) and HOMO-2 (hydrazone form) are normalized to 0 eV for convenient comparison with LUMO. First allowed and the strongest electron transitions with largest oscillator strength usually correspond almost exclusively to the transfer of an electron from HOMO \rightarrow LUMO (Figure 3 and Figure S2a-g: Supporting Information) and shows the energies of different molecular orbitals involved in the electronic transitions of these dyes in different solvents. It was observed that electronic transition in each case included HOMO \rightarrow LUMO transition for azo form and HOMO-2 \rightarrow LUMO to hydrazone form.

Molecular orbital diagrams of all the dyes in chloroform dyes are shown (Figure S3 Supporting Information). From the pictorial diagram it is clear that the electron densities in

Table 5. Observed UV-visible absorption and computed absorption spectral data at B3LYP/6-311G(d) for different dyes in chloroform

Compound	Experimental		Computed (TD-DFT)							
	$\lambda_{\text{max}}^{\text{a}}$ (nm)	ϵ Molar absorptivity ($\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)	Azo				Hydrazone			
			Vertical ^b excitation (nm)	f^{c}	Orbital contribution band gap (eV)	%D ^d	Vertical ^b excitation (nm)	f^{c}	Orbital contribution band gap (eV)	%D ^d
D1	333	94000	-	-	-	-	353.2	0.6726	H-2 \rightarrow L (95 %)	5.7
	400	36000	423.64	0.5331	H \rightarrow L (96 %)	5.6	-	-	-	-
D2	335	36000	-	-	-	-	358.84	0.8548	H-2 \rightarrow L (96 %)	6.6
	421	7400	444.28	0.4664	H \rightarrow L (96 %)	5.2	-	-	-	-
D3	342	190000	-	-	-	-	380.14	0.747	H-2 \rightarrow L (96 %)	10
	428	68000	481.79	0.4322	H \rightarrow L (97 %)	11.2	-	-	-	-
D4	331	110000	-	-	-	-	350.98	0.5399	H-2 \rightarrow L (91 %)	5.7
	392	88000	419.18	0.6672	H \rightarrow L (97 %)	6.5	-	-	-	-
D5	330	116000	-	-	-	-	355.71	0.7514	H-2 \rightarrow L (94 %)	7.2
	397	90000	431.77	0.6388	H \rightarrow L (97 %)	8.1	-	-	-	-
D6	331	178000	-	-	-	-	373.24	0.6776	H-2 \rightarrow L (95 %)	11.3
	401	124000	460.59	0.587	H \rightarrow L (98 %)	12.9	-	-	-	-

Note: $\lambda_{\text{max}}^{\text{a}}$ =Experimental maximum wavelength, Vertical^b excitation=theoretical wavelength, f^{c} =oscillator strength, %D^d=percentage deviation of theoretical and experimental wavelength.

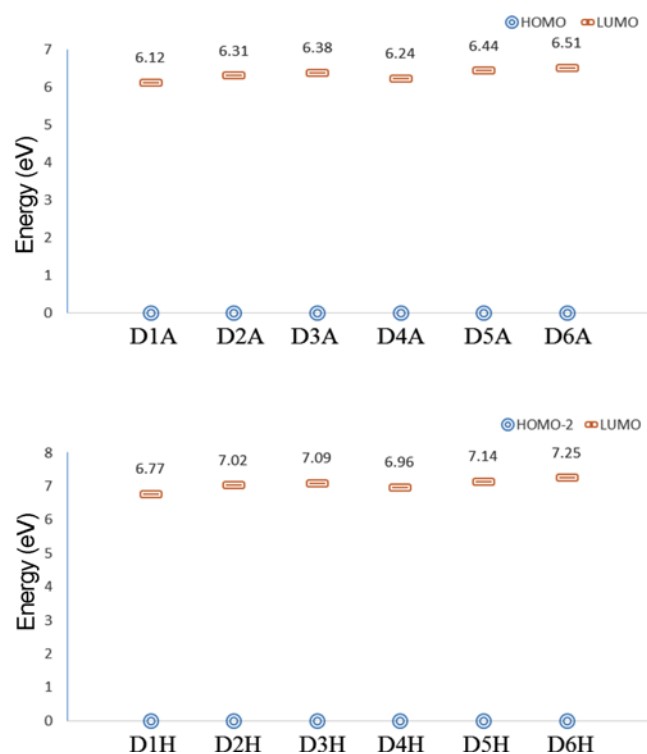


Figure 3. Energy gap between HOMO→LUMO (Azo form) and HOMO-2→LUMO (Hydrazone form) of dyes in chloroform. (Note: D=Disperse Azo dye; A=Azo form; H=Hydrazone form).

the HOMOs of all these dyes were largely located on N=N motif, while electron densities on the LUMOs were found localized throughout the molecule.

Conclusion

In this paper, we report the synthesis of 3 novel monoazo disperse dyes by diazotizing different substituted primary aromatic amines and coupling with 2-hydroxy-5-methyl acetophenone in substantial yields. The structures of the dyes were confirmed using FT-IR, ¹H-NMR, ¹³C-NMR, and HRMS spectral analysis. These yellow to red monoazo disperse dyes possess better photostability because of the photostabilizing acetyl group, which is incorporated in the dye moiety, as compared with the dyes which do not contain such an in-built photostabilizer. Also, these disperse dyes possess excellent wash fastness and moderate to good sublimation fastness on hydrophobic substrates.

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