Eco-Friendly Synthesis of 4-4′-diaminodiphenylurea, a Dye Intermediate and Direct Dyes Derived from it

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Summary: A rapid, environmental friendly and highly efficient method for the synthesis of 4-4′-diaminodiphenylurea and direct dyes derived form it has been reported. The reported method is environmentally friendly, as it doesn't involve the usage of environmentally hazardous material like phosgene and triphosgene. Novel azo dyes have been prepared by the coupling of 4-4′-Diaminodiphenylurea with various couplers. Structure elucidation of the synthesized dyes was carried out by IR, NMR, Elemental analysis, and confirmation was made by Mass Spectrometery. The dyeing performance of these dyes was assessed on cotton fabric. The dye bath exhaustion, sublimation and fastness properties were also determined. The dyed fabric showed moderate to good light fastness and very good to excellent fastness properties for washing, rubbing, perspiration, and sublimation.

Introduction

Direct dyes are widely used for dyeing of the cellulose fibers. Benzidine is widely used as an intermediate in the synthesis of most of the direct dyes [1]. The reason for using Benzidine as intermediate is that Benzidine based dyes have good colour intensity, shade and low cost of production. Unfortunately these dyes had to be abandoned when Benzidine was found to be carcinogenic [2]. Hence they had to be discontinued because of the toxicological hazards associated with them. So focus was made to search for alternate dyes, which will meet the demand of dye production and environment safety requirements. Thus extensive research has been conducted to find alternative dyes. Many approaches were made to solve the problem of replacing benzidiene based dyes. 4-4′-Diaminocarbanalide, [3] diamino-stilbene-sulphonic acid [4] and diamino-di-sulphonic acid [5] have been investigated in this context and more recently further suggestions for replacing benzidiene with other diamines have been described [6-11]. Szadowaski *et.al.,* [12] have used cyclic derivatives of benzidine. Most researchers have focused on two concepts. The first one was to focus on other classes of dyes and the second one was to use other diamines like diamino stilbene-disulphonic acid and diamino-diphenyl-amine-sulphonic acid in the dye synthesis. 4-4′-Diamino diphenyl-urea is also one of them.

Regarding the first concept, shifting totally towards other dyes doesn't usually ensure obtaining all the possible hues from duisaryl-azo-benzidiene based dyestuffs. So to fill the resultant gap in the production of direct dyes, replacement of benzidine based dyes were worked out. One such replacement is urea based dyes which contain urylene group. Dyes containing urea group have long been known and urea-based intermediates have been previously synthesized by using phosgene treatment of 5-amino-2-nitro-benzene–1-sulfonic acid followed by reduction of the resultant dinitro compounds [13] or as proposed by Peng *et. al.,* [14] by condensation of 2,4-diamine phenylene-1-sulfonic acid with *bis* (trichloro methyl) carbonate known as triphosgene in an aqueous medium. But during the process triphosgene decomposes into phosgene. So this method is also not environmentally friendly as phosgene has proven to be environmentally hazardous [15]. In the present study we report the synthesis of 4-4′-diaminodiphenylurea by an environmentally friendly method. The physical and chemical characteristics of the synthesized dyes like colour-fastness, washing fastness, perspiration fastness, sublimation fastness and rubbing fastness were examined by applying them on cotton fabric.

Results and Discussion

4-4′-Diaminodiphenylurea, has been synthesized by using acetic acid as catalyst. This is an environmentally friendly method as it has eliminated the usage of hazardous catalysts like phosgene and tri-phosgene. The yield obtained is also good and the time required is also less. Different catalysts were used in the reaction for the synthesis of 4-4′-diaminodiphenylurea (DADPU). It was seen that the appearance of the final product and also the yield of the 4-4′-diaminodiphenylurea (DADPU) was affected by the use of different catalysts. Percentage yield with different reaction times are shown in

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Table-1. Best results and yield were obtained using acetic acid as a catalyst as compared to other catalysts. Results are shown in Table-2.

Table-1: Percentage yield with different reaction times.

Reaction No	Time (h)	% age Yield
1.	24	59.24
2.	30	70.14
3.	36	72.06
4.	40	73.06

Table-2: Percentage yield by using different catalysts.

Catalyst used	% age Yield
CH_3COOH	70.14
$CH_3COOH + ZnCl_2$	65.12
$CH_3COOH + Zn$	63.17

Ten different dyes (Da-Dj) have been prepared from the said dye intermediate by coupling it with the couplers (a-j). The physical and chemical properties of the said dyes were studied and they showed good to moderate light fastness properties. The sublimation, colour-fastness and other test results are shown in Table-3 and this shows that the synthesized dyes were similar to or better that the benzidine based dyes and indicated that the synthesized direct dyes are an excellent substitute of the benzinic homologue.

ρ-Phenylenediamine easily oxidizes under the normal conditions during the progress of the reaction. So previously the synthesis of 4-4′-diaminodiphenylurea (DADPU) [16] was carried out in nitrogen atmosphere and de-aerated water conditions that increases the cost of production. In the present work $NaHSO_3$ has been used instead of nitrogen atmosphere and it was seen that no oxidation of ρ-phenylenediamine took place during the reaction. Thus the use of nitrogen atmosphere was also eliminated in the current study. Moreover, the residue can be easily removed from the product by thorough washing with water, as they are water-soluble.

Experimental

General

All the chemicals used in the dyes synthesis were obtained from Sigma-Aldrich and Acros Organics and were used as such. Melting points were taken on a Gallenkemp melting point apparatus and are uncorrected. Elemental analysis was performed with Perkin Elmer CHNS Analyser instrument. IR spectra were recorded in cm^{-1} on Schimadzu FT-IR 8400. Mass Spectra were taken on Jeol D-3000 Spectrometer. ^{1}H-NMR spectra were recorded on Brucker AC-300MHz NMR instrument and chemical shifts were reported in ppm relative to internal Me_4Si as internal standard. The UV absorption spectra were recorded on a Cecil 2000 UV-VIS spectrometer.

Synthesis of 4-4′-Diamino-diphenyl Urea

5.4 g (0.05 mol) of ρ-Phenylene-diamine and 3.6 g (0.06 mol) of urea were weighed and were put in a round bottom flask. Added 50 mL of water into the round bottom flask and placed on a hot stirring plate. 3.0 mL of 39% $NaHSO_3$ was added and stirring was continued. Added 25 mL of glacial acetic acid into it and the contents of the flask were refluxed with continuous stirring at a constant temperature of 102 °C. After reflux time of 24 h the product was filtered using Whatman 40 filter paper with the help of vacuum filtration assembly. The filtered cake was washed thoroughly first with normal water and then with hot distilled water to remove residual urea.

Spectral and Analytical data of 4-4′-Diamino-diphenyl Urea

I.R. ν_{max} (KBr/cm^{-1}), 3357 (NH), 1695 (C=O), and 1605 (C=C). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ (ppm): 7.82 (s, 1H, NH), 7.43 (d, 2H, J = 5.44 *Hz*, Ar-H), 7.33 (d, 2H, J = 5.11 *Hz*, Ar-H), 5.82 (s, 2H, NH_2). **EI MS** (m/z), 241 (100%), 225 (48%), 147 (26). **CHN** Anal. Calcd for $C_{13}H_{14}N_4O$: C, 64.10; H, 5.87; N, 23.13; O, 6.97 %. Found: C, 63.17; H, 5.86; N, 20.31; O, 6.95 %.

The same reaction was repeated under the same conditions but changing the reflux time to 30 h, 36 h and 40 h. The yield of 4-4′-Diaminodiphenylurea obtained under the different reflux times is shown in the Table-1.

Similarly the reaction was carried out using CH_3COOH, $ZnCl_2$ + CH_3COOH and Zn + CH_3COOH as catalysts keeping the reaction time of 36 h. The results are shown in Table-2.

Synthesis of Dye Da

Diazotization

3.1 g (0.012 mol) of 4-4′-Diamino-diphenyl urea (DADPU) Fig. 1 was taken in 250 mL beaker and 30 mL of distilled water was added into the beaker. Added into it 6.7 mL of 37 % fuming HCl. The contents of the beaker were stirred vigorously and the temperature of the beaker was reduced to 0 °C with the help of ice bath. At 0 °C $NaNO_2$ (9.5 mL, 20

%) was added drop wise with continuous stirring for a period of 30-minutes. The diazotized product (Fig. 2) was stirred continuously for a period of 20 minutes. Destroyed excess HNO_2 using 10 mL of 20% urea solution.

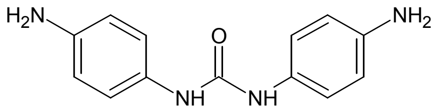


Fig. 1: (4-4′-Diamino-diphenyl urea).

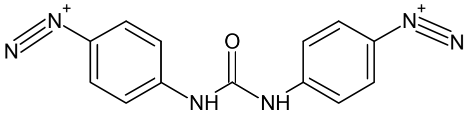
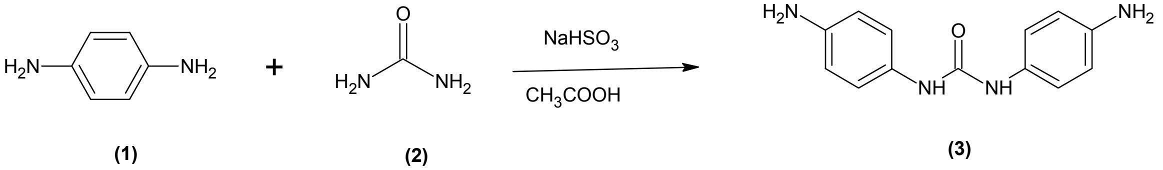


Fig. 2: (Diazotized 4-4′-Diamino-diphenyl urea).

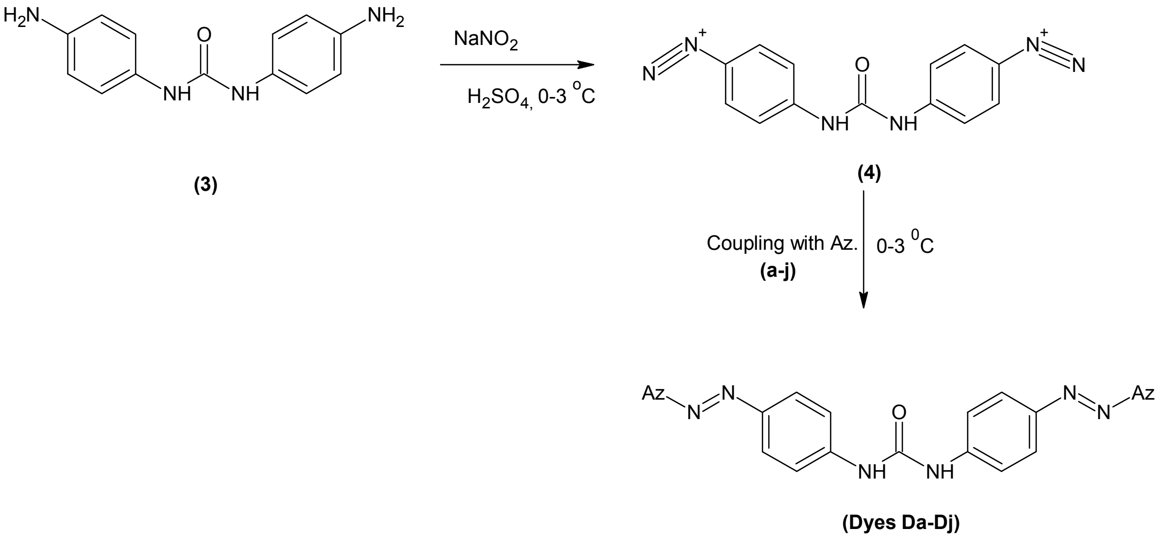
Coupling Step

9.65 g (0.005 mol) H-acid was stirred in 50 mL water, and NaOH (20 %) was added drop wise with continuous stirring till all the H-Acid dissolves. The solution was added drop wise to the diazotized solution for a period of two hours and the contents of the flask were stirred continuously for half an hour. The pH of the solution was increased up-to 9-11 and the product was stirred vigorously for a period of 3 h.

Dye was precipitated by the addition of NaCl. The obtained paste was transferred into a china dish and excess water was evaporated. The obtained dye was allowed to be dried in oven overnight at the temperature of 60 °C and then purified by column chromatography. It was performed using column packed with neutral alumina and the mobile phase for separation was dichloromethane and methanol (2:1). The separated dye was recrystalized from ethanol. Dye obtained was ground and stored in the airtight container.

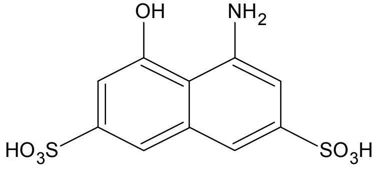
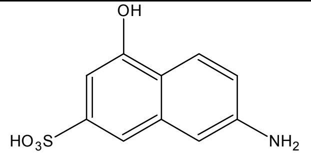
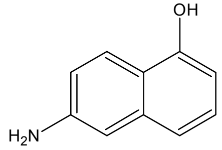
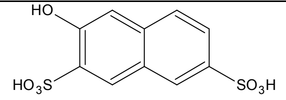
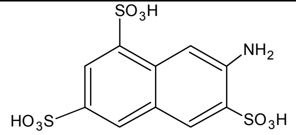
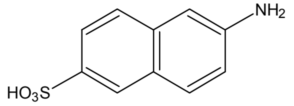
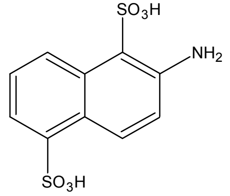
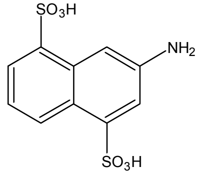
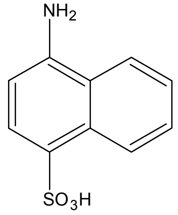
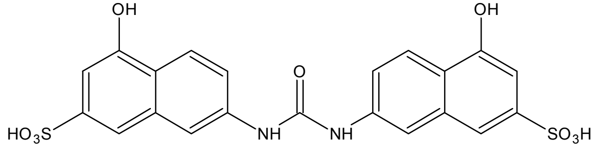


Scheme 1: (Synthesis of Dye Intermediate DADPU).



Scheme 2: (Synthesis of Dyes Da-Dj from the Dye Intermediate DADPU).

where Az =
(Couplers a-j)

 H-acid (a)	 J-acid (b)
 N-acid (c)	 R-acid (d)
 K-acid (e)	 Bruner acid (f)
 Sulfo-tobias-acid (g)	 C-acid (h)
 Lauret acid (i)	 Urea of J-acid (j)

Synthesis of Dyes Db-Dj

The synthesis of dyes Db-Dj was carried out according to the method described previously for the synthesis of dye Da. Homogeneity of the purified dye was confirmed by Chromatography [17, 18]. The synthesized dyes were characterized by NMR, MS Spectrometry and Elemental analysis. Results are shown in Table-3 and 4.

Dyeing of Cotton Fabric with Dyes (Da-Dj)

Cotton fabric was immersed in a bath containing dye solution (based on fabric weight). Bath was heated to 95 °C and stirring continued. After 10 minutes 7 g of NaCl was added into the dye bath and stirring continued. Bath was maintained at this temperature for 1 h, then heated to boil and maintained at this temperature for more 10 minutes. Fabric was removed from dye bath and dried at room temperature. Absorption data and light fastness properties of the dyes are shown in the Table-5 and 6.

Colour and Spectral Properties of Dyes Fastness Properties

The fastness to light sublimation and perspiration was assessed in accordance with BS-1006-1978. The rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with ATCC-1961 and the wash fastness test in accordance with IS-765-1979. Details of the various fastness tests are mentioned below;

Table-3: Characterization of synthesized dyes by FT-IR, NMR, and MS spectrometer.

Dye	Spectral data
Da	IR (cm^{-1} KBr) 3429, 3381 (NH$_2$), 3144 (NH), 1688 (C=O). ^{1}H-NMR (DMSO-d_6) 5.14 (s, 1H, -OH), 6.22 (s, 2H, -NH$_2$), 6.02 (s, 1H, -NH-), 6.36-7.47 (m, 3H, Ar-H), 7.53 (d, 2H, J = 7.1 *Hz*, Ar-H), 7.43 (d, 2H, J = 6.8 *Hz*, Ar-H). EI MS (m/z), 901 (100), 581 (48), 321 (36), 455 (25), 443 (18).
Db	IR (cm^{-1} KBr) 3439, 3383 (NH$_2$), 3145 (NH), 1698 (C=O). ^{1}H-NMR (DMSO-d_6) 5.65 (s, 1H, -SO$_3$H), 6.32 (s, 1H, -OH), 6.37 (s, 2H, NH$_2$), 6.17-7.10 (m, 4H, Ar-H), 7.51 (d, 2H, J = 7.1 *Hz*, Ar-H), 7.33 (d, 2H, J = 6.8 *Hz*, Ar-H). EI MS (m/z), 741 (100), 501 (57), 397 (48), 344 (37), 239 (21).
Dc	IR (cm^{-1} KBr) 3439, 3383 (NH$_2$), 3145 (NH), 1699 (C=O). ^{1}H-NMR (DMSO-d_6) 5.34 (s, 1H, -OH), 6.19 (s, 1H, -NH-), 6.53-7.47 (m, 5H, Ar-H), 7.82 (s, 2H, -NH$_2$), 7.63 (d, 2H, J = 7.0 *Hz*, Ar-H), 7.43 (d, 2H, J = 6.9 *Hz*, Ar-H). EI MS (m/z), 581 (100), 422 (63), 347 (54), 235 (41), 235 (18).
Dd	IR (cm^{-1} KBr), 3440, 3382 (NH$_2$), 3145 (NH), 1698 (C=O). ^{1}H-NMR (DMSO-$d_6^{)}$ 3.12 (s, 1H, -OH), 5.16 (s, 1H, -SO$_3$H), 6.19 (s, 1H, -NH-), 7.46-7.87 (m, 4H, Ar-H), 7.47 (d, 2H, J = 7.1 *Hz*, Ar-H), 7.35 (d, 2H, J = 6.8 *Hz*, Ar-H). EI MS (m/z) = 871 (100), 567 (63), 381 (55), 304 (47), 201 (31).
De	IR (cm^{-1} KBr) 3439, 3383 (NH$_2$), 3142 (NH), 1698 (C=O). ^{1}H-NMR (DMSO-d_6) 5.21 (s, 1H, -SO$_3$H), 6.16 (s, 1H, -NH-), 7.36-7.87 (m, 3H, Ar-H), 7.43 (d, 2H, J = 7.2 *Hz*, Ar-H), 7.25 (d, 2H, J = 6.7 *Hz*, Ar-H). EI MS (m/z), 1029 (100), 827 (77), 385 (61), 201 (33).
Df	IR (cm^{-1} KBr) 3439, 3363 (NH$_2$), 3144 (NH), 1699 (C=O). ^{1}H-NMR (DMSO-d_6) 5.81 (m, 2H, -NH$_2$), 6.16 (s, 1H, -NH-), 6.21 (s, 1H, -SO$_3$H), 7.34-7.89 (m, 4H, Ar-H), 7.44 (d, 2H, J = 7.1 *Hz*, Ar-H), 7.23 (d, 2H, J = 6.9 *Hz*, Ar-H). EI MS (m/z), 709 (100), 487 (46), 413 (33), 297 (21), 221 (16).
Dg	IR (cm^{-1} KBr) 3449, 3384 (NH$_2$), 3140 (NH), 1698 (C=O). ^{1}H-NMR (DMSO-d_6), 5.21 (s, 1H, -SO$_3$H), 6.14 (s, 1H, -NH-), 7.81 (d, 2H, -NH$_2$), 7.37-7.91 (m, 4H, Ar-H),7.59 (d, 2H, J = 7.3 *Hz*, Ar-H), 7.38 (d, 2H, J = 6.9 *Hz*, Ar-H). EI MS (m/z), 869 (100), 556 (56), 490 (50), 379 (42), 303 (31).
Dh	IR (cm^{-1} KBr) 3429, 3373 (NH$_2$), 3135 (NH), 1698 (C=O). ^{1}H-NMR (DMSO-d$_6$) 5.62 (s, 1H, -SO$_3$H), 6.14 (s, 1H, -NH-), 7.61 (s, 2H, -NH$_2$), 7.96-8.04 (m, 4H, Ar-H), 7.48 (d, 2H, J = 7.3 *Hz*, Ar-H), 7.31 (d, 2H, J = 6.9 *Hz*, Ar-H). EI MS (m/z), 869 (100), 561 (48), 409 (26), 304 (18).
Di	IR (cm^{-1} KBr) 3439, 3383 (NH$_2$), 3145 (NH), 1698 (C=O). ^{1}H-NMR (DMSO-d_6) 6.14 (s, 1H, -NH-) 7.62 (s, 1H, -SO$_3$H), 7.65-7.82 (m, 4H, Ar-H), 7.85 (s, 2H, -NH$_2$), 7.48 (d, 2H, J = 7.3 *Hz*, Ar-H), 7.31 (d, 2H, J = 6.9 *Hz*, Ar-H). EI MS (m/z), 709 (100), 487 (54), 413 (35), 221 (16),
Dj	IR (cm^{-1} KBr) 3439, 3382 (NH$_2$), 3146 (NH), 1699 (C=O). ^{1}H-NMR (DMSO-d_6) 5.42 (s, 1H, -SO$_3$H), 6.19 (s, 1H, -NH-), 6.81 (s, 1H, -OH), 7.66-8.04 (m, 9H, Ar-H), 7.51 (d, 2H, J = 7.1 *Hz*, Ar-H), 7.33 (d, 2H, J = 6.8 *Hz*, Ar-H). EI MS (m/z), 1271 (100), 765 (54), 661 (43), 609 (33) 505 (23).

Table-4: Characterization data of the synthesized dyes.

Dye	C		H		N		O		S	
	% Calc.	% Found	% Calc.	% Found	% Calc.	% Found	% Calc.	% Found	% Calc.	% Found
Da	53.32	53.01	3.53	3.42	15.09	14.85	19.39	19.21	8.63	8.58
Db	43.92	43.87	2.90	2.72	12.91	12.65	26.39	26.21	14.21	14.08
Dc	68.03	67.87	4.51	4.42	19.09	18.95	8.24	8.21	----	----
Dd	45.51	44.97	2.77	2.62	9.63	8.05	27.49	27.22	14.72	13.18
De	38.44	37.87	2.54	2.12	10.09	9.69	29.48	28.22	18.66	17.87
Df	55.77	55.37	3.69	3.02	15.77	15.01	15.76	14.99	9.02	8.68
Dg	45.51	44.37	3.01	2.42	12.87	11.75	23.80	22.11	---	----
Dh	45.51	44.37	3.01	2.52	12.87	11.87	23.80	21.91	---	----
Di	55.77	54.37	3.67	3.02	15.77	15.65	15.76	15.02	4.02	3.68
Dj	51.88	50.37	3.17	2.62	11.63	10.55	23.88	22.28	10.08	13.58

Table-5: Yield, physical and analytical data of the synthesized dyes.

Dye	Mol. formula	%Yield	M.P (°C)	λ_{max}	log ε	% E
Da	$C_{33}H_{26}O_9N_8S_2$	78	219-220	536 nm	5.12	78%
Db	$C_{33}H_{26}O_{15}N_8S_4$	72	244	559 nm	5.38	76%
Dc	$C_{33}H_{26}O_3N_8$	72	240-241	572 nm	5.66	82%
Dd	$C_{33}H_{324}O_{15}N_6S_4$	59	205-207	560 nm	5.51	77%
De	$C_{55}H_{40}O_9N_{10}S_4$	81	234-235	660 nm	6.49	85%
Df	$C_{33}H_{26}O_7N_6S_2$	65	182-184	595 nm	5.85	77%
Dg	$C_{33}H_{26}O_7N_8S_2$	74	219-222	680 nm	6.71	79%
Dh	$C_{33}H_{26}O_7N_8S_2$	67	228-230	670 nm	6.68	82%
Di	$C_{33}H_{26}O_{17}N_8S_2$	88	243	490 nm	4.70	81%
Dj	$C_{55}H_{40}O_{19}N_{10}S_4$	71	172	660 nm	6.52	86%

Light Fastness Test

The light fastness study was carried out using a Microscal light fastness tester having a straight mercury vapour lamp (MB/V 400W). The dyed fiber was exposed to light along with standard dye patterns of specific rating. Such standard samples are the blue wool standard manufactured by Microscal Ltd. and identified by the numerical designation 1-8. The higher the rating the better is the light fastness. The results are given in Table-6.

Wash Fastness Test

Fastness to washing was assessed using an automatic Lander-O-meter under the following conditions. The washing solution contained neutral soap at 5 g/L and soda ash 2 g/L washing temperature was 95 °C, the duration of washing was 30 minutes, the material to liquor ratio was 1:50. After washing the specimen was removed and rinsed with hot water (35 °C) until the rinsed water showed no alkalinity with phenolphthalein. It was then squeezed and air-dried. The effect on the colour was expressed and defined by reference to the international geometric grey scale. The results are shown in Table-6.

Rubbing Fastness Test

The specimen is fastened in a crockmeter, which causes a piece of standard white cloth to rub against the coloured specimen under controlled conditions of pressure and speed. The rubbing fingers are covered with white cloth, both for the dry test and wet test and slide back and forth for twenty strokes. The colour transferred to the white cloth is then compared with the gray scale. The gray scale used for the alteration of colour consisted of grade 1-5. The results are given in Table-6.

Perspiration Fastness Test

A specimen of the textile in contrast with the specified adjacent fibers is treated in two different solutions containing histidine, drained and placed in between two plates of 11.5 x 6 cm size and of 0.15 cm thickness under the pressure of a weight–piece of mass 5 kg in a testing device consisting of a stainless frame. It was kept in oven for 4 h at 37± 2 °C. The specimen and the adjacent fibers are dried separately. The change in colour of each specimen and the staining of the adjacent fibers are assessed with gray scale.

Acid Perspiration Test

The freshly prepared acids solution contained 5 g/L sodium chloride 2.2 g/L sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$) and 0.5 g/L L-hisatidine mono-hydrochloride mono-hydrate ($C_6H_9O_2N_3$ $HCl.H_2O$). The solution is brought to pH 5.5 with 0.1M acetic acid solution. The results are given in Table-6.

Alkaline Perspiration Test

The freshly prepared alkaline solution contained 5 g/L sodium chloride, 2.5 g/L disodium-hydrogen orthophosphate ($NaH_2PO_4.2H_2O$) and 0.5 g/L L-hisatidine mono-hydrochloride mono-hydrate ($C_6H_9O_2N_3$ $HCl.H_2O$). The solution is brought to pH 8 with 0.1M sodium hydroxide solution. The results are given in Table-6.

Sublimation Fastness Test

The composite specimens were placed in a heating device (Sublimation Tester Model STE) equipped with two heating plates with an electric heating system and kept there for 30 seconds at 150 ± 2 °C. The dried fiber was then removed and kept in air for 4 h. the change in colour of the specimen was assessed with gray scales. The results are shown in Table-6.

Determination of the Percentage of Exhaustion and Fixation

The dye bath exhaustion percentage (%E) of the dyed fiber is determined according to the method described and performed by Hari *et. al.,* [19 and the results are shown in Table-4.

Table-6: Fastness properties of synthesized dyes.

Dye No.	Colour shades	Light fastness	Washing fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
Da	**Purple**	**4-5**	**4**	**3-4**	**3**	**5**	**4**	**3**
Db	**Magenta**	**5**	**4**	**4**	**3-4**	**5**	**3-4**	**3**
Dc	**Mauve**	**4**	**3-4**	**3**	**3**	**4-5**	**4**	**4**
Dd	**Light Blue**	**4-5**	**4**	**3**	**3**	**5**	**3-4**	**3-4**
De	**Light Maroon**	**4**	**3**	**3-4**	**3**	**4-5**	**3-4**	**4**
Df	**Beige**	**4**	**3**	**4**	**3-4**	**5**	**3-4**	**3-4**
Dg	**Purplish Red**	**4**	**4-5**	**4**	**3-4**	**4-5**	**4**	**4**
Dh	**Reddish Brown**	**5**	**4**	**3-4**	**3**	**4-5**	**4**	**4**
Di	**Light green**	**4-5**	**3-4**	**4**	**3-4**	**5**	**3-4**	**3-4**
Dj	**Dark Maroon**	**4**	**3**	**4**	**3**	**5**	**3-4**	**4**

Conclusion

We have described a rapid, environmentally friendly highly efficient method for the synthesis of Diaminodiphenylurea based dyes as compared to the previous methods, which required the use of phosgene, triphosgene or utilized more time as compared to our method. This procedure offers several advantages including short reaction times, cleaner reaction profiles and simple experimental procedures. Moreover, the synthesized dyes showed level dyeing and good exhaustion properties and the other test results shown in Table-4 and 6 shows that the synthesized dyes are similar to or better that the benzidine based dyes and are there excellent substitutes.

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