

# Studies on the Laboratory Scale Synthesis of 4,4'-Diaminodiphenylurea and Preparation of Direct Dyes from the Compound

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**Abstract.** 4,4'-Diaminodiphenylurea has been synthesized as a potential replacement for benzidine by reaction between *p*-phenylenediamine and urea under different catalytic and reaction conditions. Reaction conditions have been optimized to obtain maximum yield of intermediates. Direct dyes have been prepared from the title compound. The synthesized dyes were used to dye cotton and leather and the colour fastness properties of the dyed cotton and leather were assessed. Results showed that the synthesized dyes have fair to good fastness properties for cotton.

**Keywords:** 4,4'-diaminodiphenylurea, benzidine substitute, direct dyes

## Introduction

The second amendment to German regulations on consumer goods states that the azo dyestuffs, which can release one or more of the listed 23 carcinogenic amines should no longer be used in dyeing of consumer goods (IARC, 1975). Several acid and direct dyes liberate harmful amines, such as benzidine, *o*-tolidine and dianisidine (benzidine derivatives) after reduction. Benzidine is both a genotoxic and harmful carcinogen (IARC, 1975; Case *et al.*, 1954; Scott, 1952). Human exposure to benzidine leading to bladder cancer has been related to the handling of the intermediate itself during the course of tetrazotization (Calogero *et al.*, 1987). Similarly, genotoxic metabolites have been isolated from the urine of animals, which had been fed with some azo dyes containing benzidine as the intermediate (Jocclion *et al.*, 1985). Due to the above stated risks, efforts were made to replace the carcinogenic benzidine and its derivatives by non-benzidine (benzidine-free) based direct dyes. Amide derivatives of the iso- and terephthalic acid (Wajciechowski and Gumulak, 2003), and iso- and terephthalic acid as such, have been used in the synthesis of direct dyes (Wajciechowski *et al.*, 2003). Also, benzidine substituted intermediates, and dyes based on them, have been synthesized in order to overcome the mutagenicity of benzidine (Gong *et al.*, 2002).

In this regard, 4,4'-diaminodiphenylurea (DADPU) has been proposed as a replacement for benzidine (Zhang, 1995), and it has been used to prepare direct dyes. DADPU contains ureylene group (-NHCONH-). 4,4'-Diaminodiphenylurea is normally synthesized using phosgene. Triphosgene has also been used as a substitute for phosgene to prepare urea con-

taining intermediates having ureylene group (Shi *et al.*, 1998; Peng *et al.*, 1996). Keeping in view the toxicity of phosgene and triphosgene, DADPU has been prepared in the present work using *p*-phenylenediamine and urea. The method is economical and reliable, but requires very long reaction time. Also, in the present work, the optimization of the process has been carried out under variable reaction conditions, such as reflux time, and by using different catalysts, which have resulted in better yield of the final DADPU product. DADPU has been further used to prepare direct dyes. Structure of DADPU is shown in Fig. 1(a).

## Materials and Methods

*p*-Phenylenediamine (5.4 g), urea (3.6 g) and water (50.0 ml) were transferred to a flat bottom flask, and stirred on a hot plate. NaHSO<sub>3</sub> (39%; 3.0 ml) was added to the flask and stirring continued. Glacial acetic acid (2.5 ml) was then added, and the contents of the flask were refluxed with continuous stirring at a constant temperature of 102 °C. After refluxing for 24 h, the product was filtered with the help of vacuum filtration apparatus, using Whatman 40 filter paper. The filtered cake was washed thoroughly, first with normal and then with hot distilled water to remove residual urea. The reaction was carried out under the same reaction conditions, but changing the reflux time to 30, 36 and then 40 h. The yields of the DADPU obtained under different refluxing periods are shown in Table 1. The reaction was similarly carried out using ZnCl<sub>2</sub> + CH<sub>3</sub>COOH, and Zn + CH<sub>3</sub>COOH as catalysts, keeping the reaction time of 30 h constant. Physical appearance and the yield of the final products varied under different catalytic conditions as shown in Table 2.

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**Table 1.** Yield of 4,4'-diaminodiphenylurea (DADPU) under different periods of reaction time

Reaction time (h)	Yield (%)
24	59.24
30	70.14
36	72.06
40	73.09

**Table 2.** Yield and appearance of 4,4'-diaminodiphenylurea (DADPU) obtained after the constant reflux time of 30 h, using different catalysts

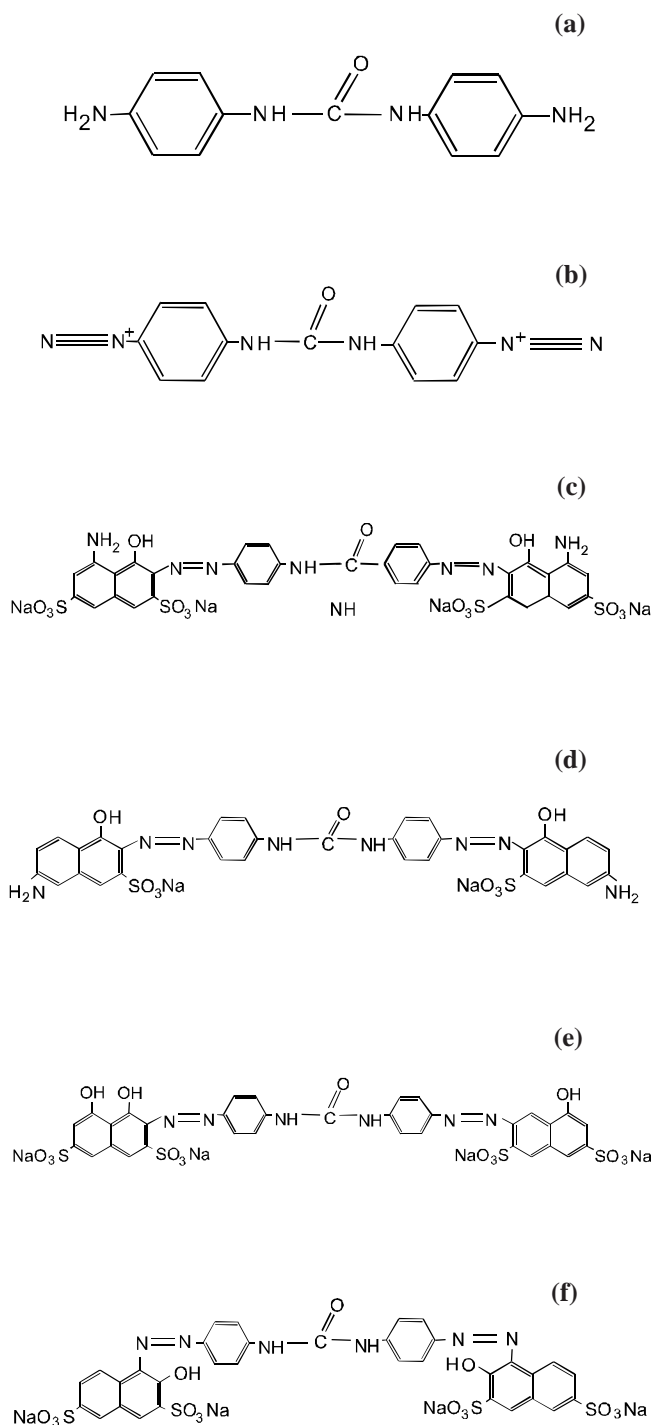
Catalyst	Appearance of DADPU	Yield (%)
CH <sub>3</sub> COOH	colourless with very light mauve tinge	70.14
CH <sub>3</sub> COOH + ZnCl <sub>2</sub>	mauve with bluish tinge	65.12
CH <sub>3</sub> COOH + Zn	mauve with greyish tinge	63.17

**Synthesis of dye-1. Tetrazotization step.** DADPU (3.1 g), distilled water (30.0 ml) and 37% fuming HCl (6.7 ml) were transferred to a 250 ml beaker. The contents of the beaker were stirred vigorously and then cooled to 0 °C with the help of ice around the beaker. At 0 °C, 20% NaNO<sub>2</sub> (9.5 ml) was added dropwise for over 30 min by keeping the contents of the beaker in continuous stirring position. Stirring of the tetrazotized product was continued for further 20 min. Excess HNO<sub>2</sub> was neutralized using 10.0 ml of 20% urea solution. The tetrazotized product is shown in Fig. 1(b).

**Coupling step.** H-acid (1-amino-8-naphthol-3,6-disulfonic acid; 9.65 g) was stirred in 50.0 ml water and NaOH (20%) was added to it dropwise, with continuous stirring till all the H-acid dissolved. This solution was added dropwise over 2 h to the tetrazotized solution of DADPU and then the reaction mixture was stirred for further one h at 0-5 °C and pH 4-6. The pH of this solution was increased to 9.0-11.0, and the product was stirred vigorously for further 3 h. Dye was precipitated by the addition of NaCl. The paste so obtained was transferred to a china dish and the excess water was evaporated. The dye obtained was ground and stored in an air-tight container. The structure of the dye (**dye-1**) is shown in Fig. 1(c).

**Synthesis of dye-2. Tetrazotization step.** Tetrazotization of DADPU was conducted as described for **dye-1**.

**Coupling step.** J-acid (2-amino-5-naphthol-7-sulfonic acid; 6.8 g) was stirred in 50.0 ml water and NaOH (20%) was added to it dropwise with continuous stirring till all the J-acid

**Fig. 1.** (a) Chemical structure of 4,4'-diaminodiphenylurea (DADPU)- the parent compound for the synthesis of direct dyes; (b) the tetrazotized product of DADPU; (c) the chemical structure of **dye-1**; (d) the chemical structure of **dye-2**; (e) the chemical structure of **dye-3**; (f) the chemical structure of **dye-4**.

dissolved. This solution was added dropwise over 1.5 h to the tetrazotized solution of DADPU and then the reaction mixture was stirred for further one h at 0-5 °C and pH 4-6. The pH of this solution was increased to 9.5-11.5 and the product was stirred vigorously for further 4 h. The dye was precipitated by the addition of NaCl. The dye paste so obtained was transferred to a china dish and the excess water was evaporated. The dye obtained was (**dye-2**) ground and stored in an air-tight container. Structure of the dye (**dye-2**) is shown in Fig. 1(d).

**Synthesis of dye-3. Tetrazotization step.** This step was the same as described for **dye-1**.

**Coupling step.** Chromotropic acid (12.3 g) was stirred in 50.0 ml water and NaOH (20%) was added to it dropwise with continuous stirring till all the chromotropic acid dissolved. The resulting solution was added dropwise over 2.0 h to the tetrazotized solution of DADPU and the reaction mixture was then stirred for further two h at 0-5 °C and pH 3-5. The pH of this solution was increased to 6.0-8.0, and the product was stirred vigorously for further 4 h. The dye was precipitated by the addition of NaCl. The dye paste was transferred to a china dish and the excess water was evaporated. The dye (**dye-3**) obtained was ground and stored in an air-tight container. The structure of the (**dye-3**) is shown in Fig. 1(e).

**Synthesis of dye-4. Tetrazotization step.** Tetrazotization step was the same as described for **dye-1**.

**Coupling step.** R-acid (2-naphthol-3,6-disulfonic acid; 9.25 g) was stirred in 50.0 ml water and NaOH (20%) was added to it dropwise with continuous stirring till all the R-acid dissolved. The resulting solution was added dropwise, over 2 h, to the tetrazotized solution of DADPU and the reaction mixture was then stirred for further one h at 0-5 °C and pH 4-6. The pH of this solution was increased to 9.0-11.0, and the product was stirred vigorously for further 4 h. The dye was precipitated by the addition of NaCl. The dye paste so obtained was transferred into a china dish and the excess water was evaporated. The dye (**dye-4**) obtained was ground and stored in an air tight container. Structure of the dye (**dye-4**) is shown in Fig. 1(f).

**Dyeing procedure. Dyeing of cotton.** The following conditions were used: depth of shade 1%; dye concentration 1%; liquor ratio 1: 50.

Cotton fabric was immersed in a bath containing the dye solution (based on fabric weight). Bath was heated to 95 °C with continuous stirring of the contents of the bath. After 10 min, NaCl (7.0 g) was added to the dye-bath and stirring was continued. Bath was maintained at this temperature for 65 min,

then heated to boil and maintained at this temperature for further 10 min. Fabric was removed from the dye-bath and dried at room temperature. Absorption data and colour fastness properties of the dyes are shown in Table. 3.

**Dyeing of leather.** The synthesized dyes were used to dye buffalo split leather and sheep crust leather. A total of 5% was dyed on the weight of buffalo split and sheep crust leather (3.0% penetration followed by 2.0 % topping). Properties observed in both the cases are shown in Tables 4 and 5 for buffalo split leather and sheep crust leather, respectively.

**Analytical measurements.** Infra red (IR) spectrum (KBr) of DADPU was taken using IR spectrophotometer and is shown in Fig. 2. Analytical data for DADPU is shown in Table 6.

## Results and Discussion

**The use of NaHSO<sub>3</sub> (39%) as reducing agent.** DADPU is oxidized under normal conditions. Therefore, the synthesis in prior studies of DADPU was carried out in deoxygenated conditions and required N<sub>2</sub> atmosphere (Spiewak, 1977). In the present work, NaHSO<sub>3</sub> was used as the reducing agent. It was observed that white DADPU can be obtained using a small amount of NaHSO<sub>3</sub>, thus eliminating the need for the use of deaerated water and N<sub>2</sub> protection. Moreover, the residual NaHSO<sub>3</sub> can be easily removed from DADPU through washing the sample, as it is soluble in water.

**The use of different catalysts.** Different catalysts were used in the reaction for the synthesis of DADPU. It was observed that the appearance as well as the yield of DADPU changed when different catalysts were used. Best results were obtained when CH<sub>3</sub>COOH was used as the catalyst. By using CH<sub>3</sub>COOH, as the catalyst, better yield and appearance of the target compound was obtained as compared to other catalysts. Results obtained during the investigation are shown in Table 2.

**Table 3.** The dye absorption data and fastness properties\* on cotton in respect of the dyes synthesized from 4,4'-diaminodiphenylurea (UADPU)

	Dyeing characteristics			
	Dye-1	Dye-2	Dye-3	Dye-4
$\lambda_{max}$	536	559	572	560
Washing (with soap)	4-5	4-5	4-5	3-4
Perspiration	4-5	4-5	4-5	4
Dry rubbing	4-5	4-5	4-5	4
Water	4-5	4	4	3-4
Sunlight	4-5	4-5	4	4

\* Grey scale for assessing staining (ISO-105-A03)

**Table 4.** Dyeing characteristics of different dyes synthesized from 4,4'-diaminodiphenylurea (DADPU); material: buffalo split leather; thickness: 1.9-2.0 mm; article: buffalo garment leather

Parameters	Dye-1	Dye-2	Dye-3	Dye-4
Colour depth	excellent	good	good	fair
Rub fastness	poor	fair	good	good
Wash fastness	poor	poor	poor	poor
Light fastness	good	good	good	fair

**Table 5.** Dyeing characteristics of different dyes synthesized from 4,4'-diaminodiphenylurea (DADPU); material: sheep crust leather; thickness: 0.9-1.0 mm; article type: sheep garment leather

Parameters	Dye-1	Dye-2	Dye-3	Dye-4
Colour depth	good	poor	excellent	fair
Rub fastness	poor	fair	good	poor
Wash fastness	poor	poor	poor	poor
Light fastness	good	good	good	fair

**Table 6.** The infra red (IR) analytical (KBr) data for 4,4'-diaminodiphenylurea (DADPU)

Functional groups	IR (KBr) $\text{cm}^{-1}$
CO (carbonyl group)	1593, 1545
NH (amide group)	3262
CH (bending)	1506

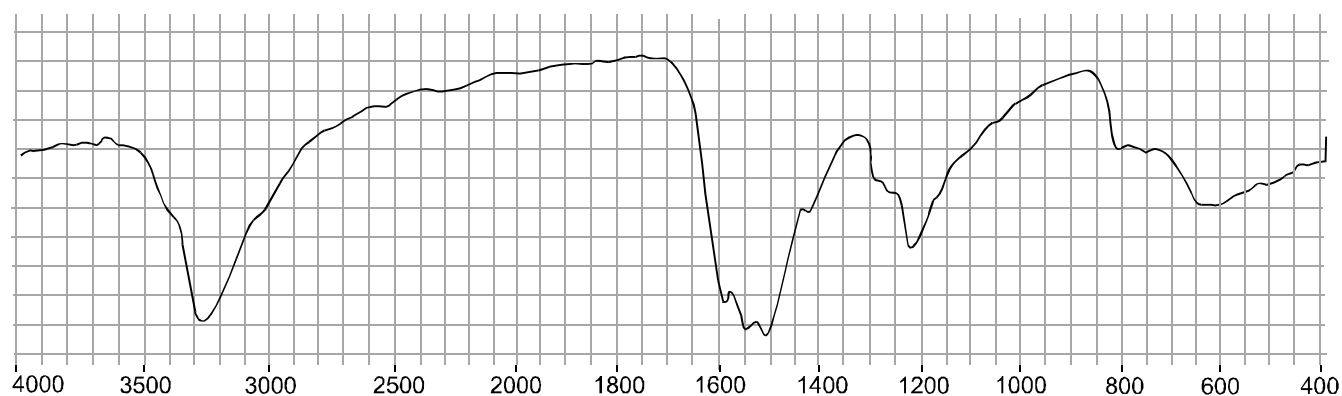
It was observed that the yield of DADPU was improved by increasing the reaction time. Synthesis of DADPU was carried out at the reflux time of 24, 30, 36 and 40 h. Results obtained are shown in Table 1. It was observed that 59% yield was obtained after the reflux of 24 h. When the reaction time was increased from 24 to 30 h, 70% yield was obtained. After the reflux of 36 h, yield increased to 72%. By increasing the reaction time from 36 to 40 h, the increase was only 1%, making the 36 h reflux period as the optimal reaction time.

## Conclusion

The different dyes synthesized from DADPU as the starting compound were used to dye cotton fabric and leather. It was concluded from the results obtained that dyes had good fastness properties for cotton fabric, whereas poor fastness properties were observed in the case of leather (Tables 3, 4, 5). Based on these observations, it can be concluded that the synthesized dyes had fair to good fastness properties for cotton.

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**Fig. 2.** Infra red spectrum (KBr) of 4,4'-diaminodiphenylurea (DADPU).

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