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Studies on the synthesis of 4,4′-diaminodiphenylurea and direct dyes derived therefrom

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Abstract

4,4′-Diaminodiphenylurea has been synthesized as a potential substitute for benzidine, by a reaction between urea and *para*-phenyldiamine in water. The synthesis is straightforward and economical, and produces a high quality product. The title compound was used to prepare direct dyes for cotton. The color and fastness properties of the dyed fabric were assessed, and the results showed that the dyes have good substantivity and light fastness.

Keywords: 4,4′-Diaminodiphenylurea; Benzidine replacement; Direct dyes

1. Introduction

Since it is well known that benzidine is a carcinogenic compound, there has been considerable interest in the synthesis of non-benzidine-based direct dyes. In this regard, 4,4′-diaminodiphenylurea (DADPU) (Fig. 1) has been proposed as a replacement for benzidine [1], and it has been used to prepare disazo dyes. DADPU is normally synthesized using phosgene or urea. In view of the toxicity of phosgene, the former method is not practical. While, the latter method is safer and more economical, it requires a very long reaction time.

In the present paper, the synthesis of DADPU from urea has been improved, and the diamine has been used to make direct dyes.

2. Experimental

2.1. Synthesis of DADPU

A mixture of urea (1.8 g), *para*-phenylenediamine (5.4 g), $NaHSO_3$ (0.4 g), HOAc (1 ml) and H_2O (50 ml) was stirred at reflux for 36 h. The reaction mixture was cooled to room temperature, and the product was filtered. Washing with hot water removed residual urea and *para*-phenylenediamine, affording a product of 5.95 g (96.3%) with a purity level of 97.1%.

2.2. Synthesis of dye *I*

Diazotization step: DADPU (6.2 g) was dissolved in HCl (10.7 ml, 36%) and water (50 ml) was added. At 0 °C $NaNO_2$ (3.4 g, 20%) was added dropwise for over 30 min. The reaction mixture was stirred at 0–2 °C for 40 min, and excess nitrous acid was destroyed with urea.

First coupling step: 2,5-Dichloro-4-(4,5-dihydro-3-methyl-5-oxo-1*H*-pyrazol-1-yl)-benzene sulfonic acid (9.2 g) was dissolved in water (30 ml) and NaOH (20%) was added until pH 7–8 was reached. The solution was added dropwise to the solution of diazotized DADPU prepared above. The addition required 30 min and the reaction was stirred for 1 h at 0–5 °C and pH 6.1–6.5.

Second coupling step: A solution of J-acid (6.5 g), water (50 ml), and NaOH (3 ml, 20%) was added dropwise, over 1 h, to the solution from the first coupling step, and the reaction mixture was stirred for

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Fig. 1. DADPU structure.

l h at 0–5 °C and pH 8–10. NaCl was added to precipitate the product, and the filtered cake was dried below 60 °C to give 16.5 g of dye **I**.

2.3. Synthesis of dye *II*

Diazotization of DADPU was conducted as described above in Section 2.2.

First coupling step: A solution of H-acid (9.6 g), water (20 ml), and NaOH (20 ml, 20%) was added dropwise, over 4 h, to the solution of diazotized DADPU, and the reaction mixture was stirred for 2 h at 0–5 °C and pH 4–6.

Second coupling step: This step was the same as the second coupling described in Section 2.2, and afforded 15.6 g dye **II**.

2.4. Synthesis of dye *III*

Diazotization of DADPU was conducted as described above in Section 2.2.

Coupling step: H-acid (19.3 g) was stirred in water (50 ml), and NaOH (20%) was added until the H-acid was completely dissolved. Diazotized DADPU was added dropwise to the solution of H-acid over 3 h at pH 8–10, and the reaction mixture was stirred for 4 h at 0–5 °C. NaCl was added to precipitate the product, and the altered cake was dried below 60 °C to give 17.6 g of dye **III**.

2.5. Dyeing procedure

Depth of shade: 1%
Dye concentration: 1 g/500 ml
Liquor ratio: 50:1

Cotton fabric was immersed in a bath containing dye solution (based on the fabric weight), Na_2SO_4 (10%), and HOAc (1%), at 40 °C. The bath was heated to 96–95 °C over 30–40 min and then heated to boil for over 5 min. The bath was maintained at the boil for 10 min, the fabric was removed, rinsed with 50 °C water, and dried at room temperature.

Table 1
The effects of acid catalysts on the synthesis of DADPU[a]

Expt. no.	Catalysts	Purity (%)	Yield (%)
1	None	98.0	47.7
2	$ZnCl_2$	88.8	74.0
3	HCl	90.5	78.4
4	HOAc	98.0	86.0

[a] Reaction time = 24 h.

Table 2
Effects of molar ratio on the synthesis of DADPU

Expt. no.	Molar ratio[a]	Product purity (%)	Product yield (%)
5	1.0:2.0	90.5	78.4
6	1.0:2.2	86.5	84.0
7	1.2:2.0	90.4	86.4

[a] Urea:*para*-phenyldiamine.

Table 3
Effects of reaction time on the synthesis of DADPU

Expt. no.	Reaction time (h)	Purity (%)	Yield (%)
8	24	96.9	85.3
9	36	97.1	96.3
10	48	96.8	96.7

2.6. Analytical measurements

Elemental analysis was carried out with CHNCORDER MF3 TYPE instrument (Yanaco Company, Japan), IR spectra (KBr) were recorded on a Nicolet 5DX FT-IR spectrometer, and UV–VIS spectra were recorded on a CARL ZEISS JENA SPECORD spectrophotometer (Germany).

3. Results and discussion

3.1. Synthesis of DADPU

3.1.1. Use of $NaHSO_3$

Since DADPU can be easily oxidized, in prior studies, the condensation of urea and *para*-phenyldiamine was carried out in deoxygenated water and required a nitrogen atmosphere [2]. We have found that pure white DADPU can be obtained using a small amount of $NaHSO_3$ as a reducing agent, eliminating the need for deaerated water and nitrogen protection. The product can be used directly to make dyes, simplifying its use. Moreover, residual $NaHSO_3$ can be easily separated from DADPU because it readily dissolves in water.

3.1.2. Use of HOAc

In the synthesis, one molecule of urea and two molecules of *para*-phenyldiamine produce one molecule

Table 4
IR and combustion data

IR (KBr) cm^{-1}	Elemental analysis		
		Calculated (%)	Found (%)
1609.2, 1553.5 (CO)	C:	64.37	64.30
3402.9, 3301.2 (NH)	H:	5.79	5.79
3033.7, 1609.3, 1511.3 (CH)	N:	23.14	23.15

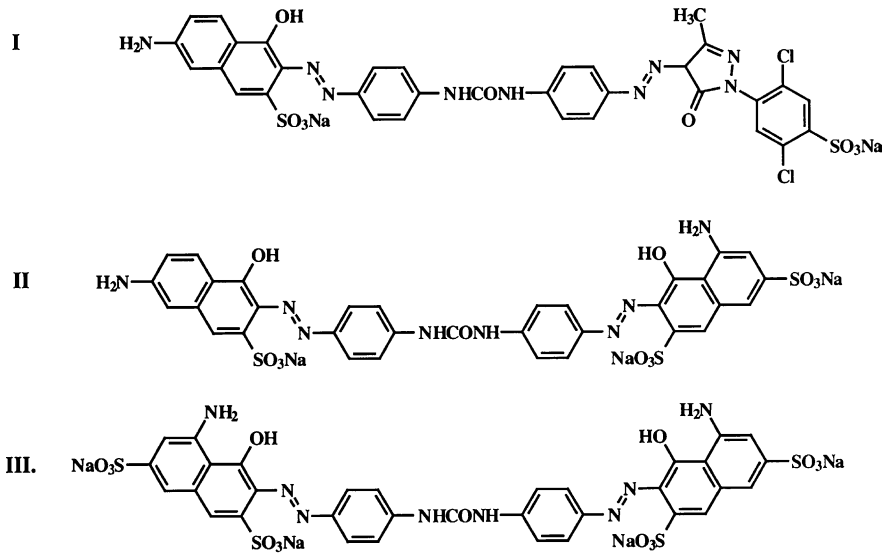

Fig. 2. Structures of dyes prepared in this study.

of DADPU and two molecules of NH_3. The reaction rate is very slow, requiring 24 h to give a 47% yield, and 72 h to give a 90% yield. It has been found that the reaction rate was accelerated when a catalyst such as $ZnCl_2$, HCl or HOAc was added [3], with HOAc especially effective in improving the reaction rate. A summary of the data is shown in Table 1.

3.1.3. Molar ratio of reactants

As anticipated, when one of the reactants was present in excess, the yield was improved. Data in Table 2 show that the optimal molar ratio of urea and *p*-phenyldiamine was 1.2:2.0. This ratio gave the highest yield, was the most economical and affordable, also providing for the use of a greater proportion of the reactant that is less expensive, and is the most easily isolated product.

Table 5
Absorption data and fastness properties[a] for **I–III** dyes on cotton

Dye no.	I	II	III
λ_{max} (nm)	490	546	562
ϵ_{max} ($\times 10^4$)	5.09	3.03	3.98
Light (1/depth)	5–6	6	5–6
Washing (soap)	4	4–5	4–5
Wool staining	3–4	4–5	4–5
Cotton staining	3–4	3–4	3–4
Perspiration	4–5	5	5
Wool staining	4	4–5	4–5
Cotton staining	3–4	4–5	4
Rubbing dry	3–4	4–5	4–5
Wet	3	3	3–4

[a] Rating scale was 1 (lowest) to 8 (highest).

3.1.4. Reaction time

To investigate the effects of reaction time, the synthesis of DADPU was carried out at 24 h, 36 h, and 48 h. The results obtained are provided in Table 3. When the reaction time was increased from 24 h to 36 h, the yield increased 11%, but when it was increased from 36 h to 48 h, only a further increase of 0.4% resulted—making 36 h the optimal reaction time.

3.1.5. DADPU characterization

Analytical data for DADPU are shown in Table 4. It is clear that analytically pure DADPU was produced.

3.2. Synthesis of direct dyes containing DADPU

Using DADPU and couplers 2,5-dichloro-4-(4,5-dihydro-3-methyl-5-oxo-1*H*-pyrazol-1-y1)-benzenesulfonic acid, J-acid and H-acid, the three direct dyes shown in Fig. 2 were obtained. Fastness properties of dyed cotton are shown in Table 5. Based on Table 5, it can be concluded that the three dyes have fair to good fastness property on cotton, fastness to light being the best property.

References

[1] Zhang J. The substitute tend for prohibited azo dyestuffs in the world. Dye Ind 1995;32(4):1 [in Chinese].
[2] Spiewak JW. Ordered aromatic copolyamide urea polymer. U.S. Patent 4,035,344. Chem Abstr 1977;87:85789h.
[3] Yidong G. Chemistry dictionary. Shanghai: Dictionary Press; 1989 [in Chinese].