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Direct dyes containing two urea groups

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Abstract

J-acid and γ-acid were condensed with tolueneisocyanate to prepare new coupling components , containing two urea groups, with similar properties to those of the known J-acid urea. The diurea dyes obtained from the new intermediates show similar properties to those of conventional phosgenated direct dyes. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Direct dyes; Phosgene; Isocyanates; *N,N′-substituted urea*

1. Introduction

Symmetric diarylureas find applications as direct dyes and intermediates used for their synthesis. There has been a growing interest in these compounds in recent years due to the fact that many direct dyes based on carcinogenic amines have been withdrawn.

So far, the only commercial process used for the production of diarylureas is the acylation of appropriate amines with phosgene. The manufacture and use of phosgene is, however, more and more restricted due to the toxicity of this compound and the general trend to eliminate chlorine compounds. The plastics industry, for instance, has undertaken various attempts to eliminate phosgene [1], 2nd it seems advisable to take up a similar search in the dyestuff industry. In this respect, the use of solid triphosgene instead of gaseous phosgene to produce urea dyes has been proposed [2]. This is, however, only a half-measure, since during the process triphosgene decomposes and emits phosgene. Several processes have been reported concerning the preparation of aromatic derivatives of urea without the use of phosgene, for example, based on urea or carbonic acid esters [3,4]:

$$2\ RNH_2 + CO(NH_2)_2 \rightarrow RNHCONHR + 2\ NH_3$$

$$2\ RNH_2 + CO(OR')_2 \rightarrow RNHCONHR + 2\ R'OH$$

However, none of these proposals has been implemented on a commercial scale since these reagents are suitable only for the preparation of simple arylureas [5] which are unsuitable for the synthesis of dyes or intermediates.

In our studies intended to eliminate phosgene, we paid attention to the possibility of preparing urea derivatives (**2**) from appropriate amines and isocyanates (**1**):

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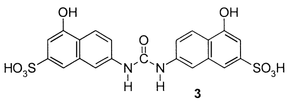
$$\underset{\mathbf{1}}{2\,RNH_2+OCNR'NCO} \rightarrow \underset{\mathbf{2}}{RNHCONHR'NHCONHR}$$

So far, the use of diisocyanates to prepare bisarylurea dyes has been confined only to the synthesis of pigments by the condensation of appropriate amino monoazo [6,7] or anthraquinone [8] compounds with aryl- or alkyldiisocyanates.

It has been recently found that with a slight modification of the synthesis conditions it is possible to prepare water soluble compounds containing two urea groups according to the same reaction scheme. The developed conditions make it possible to synthesize new coupling components containing two urea groups [9].

In the present study, the analogue of the commonly used 6-ureide-bis(1-naphthol-3-sulphonic acid (J-acid urea) (**3**) was synthesized by the condensation of 1-naphthol-6-amino-3-sulphonic acid (J-acid) (**4**) with toluene-2,4-diisocyanate (**5**) in a polar solvent medium.



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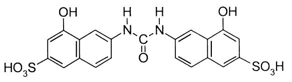

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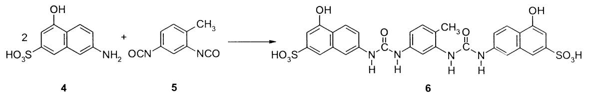
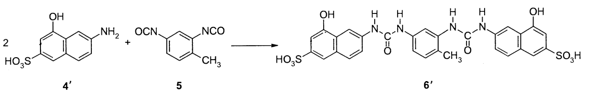
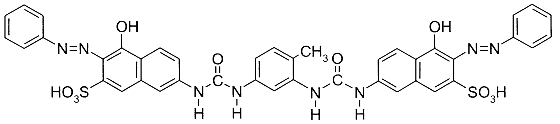


Similarly, 1-naphthol-7-amino-3-sulphonic acid (γ acid) (**4′**) was condensed with toluene-2,4-diisocyanate.



The resultant 2,4-bis(6′-ureide-1-naphthol-3′-sulpho)-toluene (**6**) and 2,4-bis(7′-ureide-1′-naphthol-3′-sulpho)toluene (**6′**) were used as coupling components to synthesize disazo direct dyes containing two urea groups. Using diazotized aniline, sulphanilic acid, 4-anisidine-2-sulphonic acid and 1-naphthylamine-5-sulphonic acid, a series of disazo dyes with two urea groups was prepared (**7**, **8**, **9**, **10** and **7′** and **10′**).



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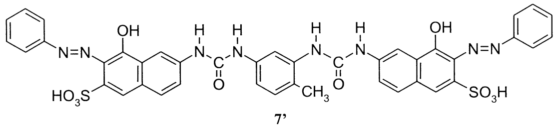

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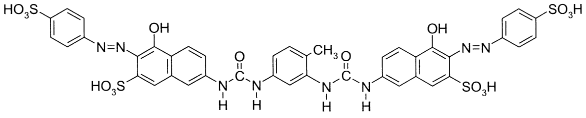

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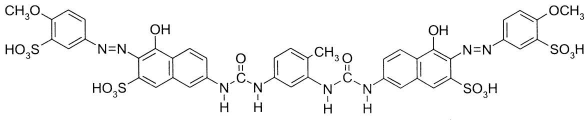

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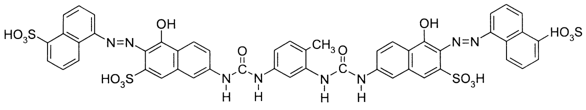

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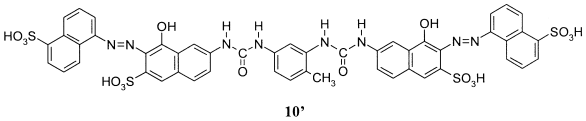

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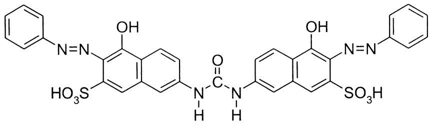
The dye exhaustion degree of the dyes onto cellulose fibres and their colour characteristics as well as dye fastness were examined. The properties of the dyes containing two urea groups (**7**, **8**, **9**, **10** and **7′**, **10′**) were compared with those of monoazo dyes containing the simplest arylamide system, prepared by coupling the same diazo components with benzoyl-J-acid (**15**, **16**, **17**, **18**) and with benzoyl-γ acid (**15′** and **18′**).



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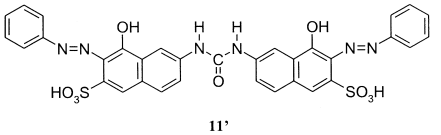

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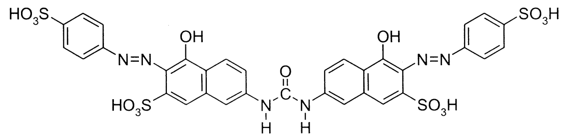

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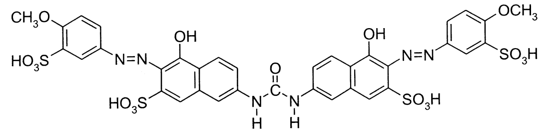

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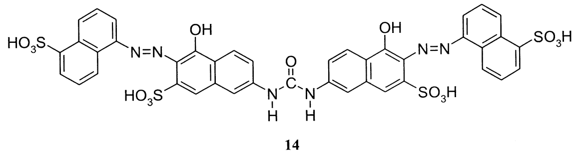

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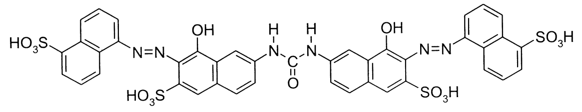

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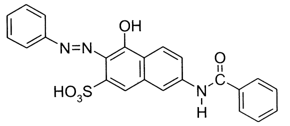

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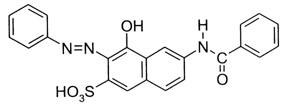

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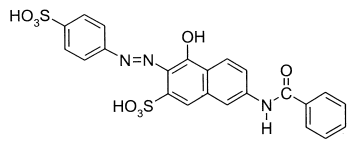

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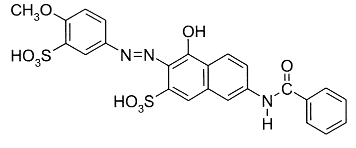

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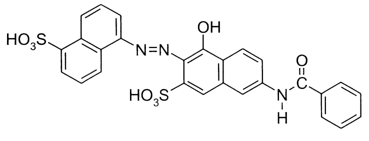

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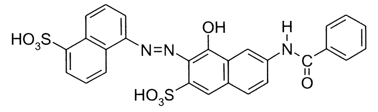

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2. Experimental

*2.1. Synthesis of 2,4-bis(6′-ureido-1′naphthol-3′-sulpho-3′)toluene (**6**) or 2,4-bis(7′-ureide-1′naphthol-3′-sulpho)-toluene (**6′**) [9].*

A suspension of 4.78 g (0.02 mol) of 6-amino-1-naphthol-3-sulphonic acid (J-acid) (**4**) or 7-amino-1-naphthol-3-sulphonic acid (γ acid) (**4′**), 1.74 g (0.01 mol) of 2,4-toluenediisocyanate (**5**) and 2.44 (0.02 mol) of 4-(*N*,*N*-dimethylamino)-pyridine (DMAP) in 50 ml of DMF was heated for 12 h at 150°C. The resultant product was separated from the solution by diluting with 800 ml of water and acidifying with HCl. After filtration, washing with water and drying, about 3.5 g of the product (**6** or **6′**) was obtained, which corresponds to a 50% yield. The product homogeneity was verified chromatography (a Whatman 1 filter paper, eluent: propanol/5% $NaHCO_3$ 2/1), while the pure product content in the precipitate was determined by titration with 0.1 M diazotized *p*-nitroaniline solution.

*2.2. Synthesis of dyes (**7-18** and **7′-18′**).*

A solution of 0.01 mol of the appropriate amine in 50 ml of water acidified with 0.025 mol HCl was diazotized at 0–5°C by adding dropwise a solution of 0.01 mol $NaNO_2$. The solution or suspension of the diazonium salt was then added dropwise to the alkaline solution of 0.005 mol **3** or **6** (or **3′** and **6′**) or 0.01 mol of benzoyl-J acid (or benzoyl-γ acid), maintaining pH 7.5–8 by adding Na_2CO_3. The dyes were separated from the solution by adding 10–20% by vol. NaCl.

2.3. Dye analysis

The homogeneity of the dyes was determined by chromatography [10] (a Whatman 1 filter paper, eluent: $MeOH/DMF/H_2O$ 3/1/1). The NaCl content in the dye samples was measured by the potentiometric method [11]. The pure dye content in samples was calculated from the sulphonic group content determined by titration with 0.005 M hyamine solution [12].

2.4. *Dye exhaustion degree*

The degree of dye exhaustion by cellulose fibres (E) was determined by dyeing samples of a bleached mercerized cotton fabric in a Roaches–Rotec dyeing apparatus, using 1% of dye in relation to fibres with addition of 0.5% Na_2SO_4 at the dye liquor at a fibre ratio 30:1. The sample was heated to 95°C in the dyebath for 2 h and dyed at this temperature for 1 h. The dyebath was then cooled to 60°C over 1 h. The dyed samples were thoroughly rinsed and dried. The degree of dye exhaustion (E) was determined by colorimetry, measuring the dye concentration in the dyebath before (c_1) and after dyeing (c_2).

$$E = \frac{c_1 - c_2}{c_1} \cdot 100\%$$

2.5. *Spectrophotometric measurements*

Standard solutions were prepared by dissolving 0.025 g of dye in 100 ml of water containing 0.04 g of Na_2SO_4. These solutions were diluted to a concentration which made measurements possible. All the solutions were stored prior to measurement for 24 h in darkness. Measurements were carried out on a Specord M40 (Zeiss-Jena) spectrophotometer, using glass cells with a thickness of 10 mm.

2.6. *Dye fastness determination*

The dye fastness was determined in accordance with Polish Standards which comply with the European Standards.

3. Results and discussion

Owing to the modification of condensation conditions of toluenediisocyanate with aminonaphtholsulphonic acids, a method has been developed for the preparation of new water soluble coupling components containing two urea groups. By condensing the quaternary ammonium salt (DMAP) of J-acid (**4**) or γ acid (**4′**) with toluene-2,4-diisocyanate (**5**) in DMF, new coupling components (**6** and **6′**) were prepared whose structure is similar to that of the commonly known J-acid urea (**3**) or the lesser known γ acid urea (**3**). By coupling these components (**6 and 6′**) with diazonium salts of aniline, sulphanilic acid, 4-anisidine-2-sulphonic acid and 1-naphthylamine-5-sulphonic acid, a series of disazo dyes with two urea groups were obtained (**7–10** and **7′** and **10′**). The dyeing, colour and performance properties of the dyes were examined and compared with those of analogous dyes containing only one urea group, prepared on the basis of J-acid urea or γ acid urea (**3 and 3′**) (**11–14** and **11′** and **14′**) as well as with the properties of monoazo dyes prepared by coupling the same diazo components with benzoyl-J-acid or benzoyl-γ-acid, containing an N-phenylamide group instead of the *N*,*N′*-diarylurea arrangement (**15–18** or **15′** and **18′**).

Comparing the colour of the dyes under investigation, it was found that dyes with a different number and type of amide groups in a molecule were characterized by a similar shade, which depends only on the diazo component used and not on the number and arrangement of amide groups in the molecule (Table 1). The absorption maxima of the dyes obtained from various coupling components but based on the same diazo components (**7**, **11** and **15** or **7′**, **11′**, **15′**; **8**, **12** and **16**; **9**, **13** and **17**; **10**, **14** and **18** or **10′**, **14′**, **18′**) differ slightly. The dyes obtained from the new coupling component (**6** or **6′**) containing two urea groups (**7–10** and **7′**, **10′**) show, however, a slight hypsochromic effect in comparison to the analogous urea dyes (**11–14** and **11′**, **14′**) and benzamide dyes (**15–18** and **15′**, **18′**). In addition, the shade of the dyeings of the diurea dyes (**7–10** and **7′**, **1′′**) is slightly duller (their spectra show a wider absorption band) in comparison to the remaining dyes. This is confirmed by the higher value of the absorption band half-width of dyes **7–10** (Table 1). Moreover, the diurea dyes (**7–10**) show a slight hypochromic effect (the molar absorption coefficient is somewhat lower than that of the remaining dyes). The hypsochromic and hypochromic effects and the somewhat dull shade are probably due to the lack of symmetry of both chromophore systems in

Table 1
Properties and exhaustion degree of dyes

Dye	Purity (%)	$\lambda_{\max}(\epsilon_{\max})$	Wideness of abs. Band	E (%)	R_f	Fastness to											
						Washing at 40°C			Rubbing		Perspiration						Light
											Acid			Alkaline			
						1	2	3	Dry	Wet	1	2	3	1	2	3	
7	98.3	485 (17700)	124	87	0.22	3–4	5	5	4–5	4	3–4	5	5	3–4	5	5	2–3
7′	97.2	515 (16500)	128	72	0.63	2–3	5	4–5	5	5	3	5	5	3	5	5	2
8	33.0	484 (43500)	125	34	0.50	4–5	5	5	5	4–5	3–4	5	5	3	5	5	2–3
9	84.0	505 (41200)	137	51	0.24	4	5	5	5	4–5	3–4	5	5	3	5	5	2–3
10	58.0	522 (31300)	136	62	0.35	3	5	5	4–5	4–5	3–4	5	5	3	5	5	2
10′	66.4	531 (21600)	184	46	0.65	3–4	5	5	5	5	3	5	5	3	5	5	1–2
11	74.3	497 (33700)	115	83	0.18	3–4	5	5	4–5	4	3–4	5	5	3–4	5	5	2–3
11′	92.6	520 (28000)	101	72	0.66	2–3	5	4–5	5	5	3–4	5	5	3–4	5	5	2–3
12	22.4	487 (50500)	102	36	0.45	4–5	5	5	5	4–5	3–4	5	5	3	5	5	2–3
13	77.6	518 (40500)	100	56	0.36	4	5	5	5	4	3–4	5	5	3	5	5	2–3
14	59.7	524 (32600)	117	59	0.48	3–4	5	5	5	4	3–4	5	5	3	5	5	2
14′	80.0	533 (24500)	147	32.5	0.68	3–4	5	5	5	4–5	3–4	5	5	3	5	5	2
15	97.1	487 (20400)	86	40	0.68	2–3	5	5	5	4	3	5	4	3	5	4	3
15′	93.0	499 (11500)	90	35	0.82	2–3	5	4–5	5	5	3	5	4–5	3	5	4	2
16	40.8	485 (17900)	88	26	0.65	4	5	5	5	4–5	3	5	5	2–3	5	4–5	2–3
17	83.3	503 (15800)	97	25	0.67	3–4	5	5	5	4–5	3	5	4–5	2–3	5	4–5	2–3
18	78.5	520 (14200)	104	42	0.65	3	5	5	5	4–5	3	5	4–5	2–3	5	4–5	2
18′	79.5	524 (14800)	103	28.5	0.75	3–4	5	5	5	4–5	3	5	4–5	2–3	5	4	1–2

1, cotton; 2, change; 3. wool.

the molecules of diurea dyes and a greater isolation of these chromophores.

The disazo diurea dyes (**7**–**10**) are characterized by a similar exhaustion degree to that of analogous urea dyes (**11**–**14**). The deviations, in both directions, by 2–5% between the exhaustion degrees of particular pairs of diurea and urea dyes (**7** and **11**; **7′** and **11′**; **8** and **12**; **9** and **13**; **10** and **14**; **10′** and **14′**) are within the measurement error limits. As expected, all the disazo dyes, both diurea (**7**–**10**) and urea (**11**–**14**) show a considerably higher affinity to cellulose fibres than analogous monoazo dyes (**15**–**18**). The increased affinity and mutual similarity of both types of disazo dyes is also indicated by the values of the chromatographic constants (R_f), which in the case of dyes **7**–**14** are similar for particular pairs of the analogues being considerably lower than the R_f values of corresponding monoazo dyes (**15**–**18**).

The dyeing fastness values of disazo dyes are almost the same for particular dye pairs. The dyeing fastness values of the disazo dyes (**7**–**14**) are mostly slightly higher than those of analogous monoazo dyes (**15**–**18**), which is consistent with general principles and justified by the higher affinity of disazo dyes.

4. Conclusions

Based on the results obtained in the present study, it can be concluded that the new group of disazo dyes containing two urea groups show similar properties to those of conventional urea dyes. Thus, the synthesis of direct dyes can be performed with the use of the condensation product of diisocyanate and J-acid (**6**) instead of J-acid urea (**3**) as coupling component, which makes it possible to avoid the use of phosgene. As expected, the corresponding of γ acid derivatives have a lower substantivity than the derivatives of

J-acid, and only in exceptional cases can they be used as direct dyes. The use of diisocyanate and the necessity to carry out the synthesis of the basic intermediate in a non-aqueous medium constitute an obstacle to a use of the new group of direct dyes. Therefore, it is worthwhile to search for simpler phosgene-free processes to prepare *N*,*N*′-diarylureas.

Acknowledgements

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