ELSEVIER

Dyes and Pigments 42 (1999) 227–235

DYES and PIGMENTS

# Iron complexed dyes based on 1,5-diaryl-3-cyanoformazanes

Małgorzata Szymczyk *, Wojciech Czajkowski, Roland Stolarski

*Department of Dyes, Technical University of Lodz, Zwirki 36, 90-924 Łódź, Poland*

Received 5 January 1999; accepted 3 March 1999

**Abstract**

In the search for more environmental friendly dyes, the synthesis of new 1:2 iron complexes of 1,5-diaryl-3-cyanoformazanes was carried out. The structure and colouristic properties of 16 new dyes and their intermediates was characterised by $^1$H NMR, FAB and UV–VIS spectroscopy. The products were used as acid dyes in the coloration of wool and polyamide fibres. Application, colouristic and fastness properties of the dyes were determined and discussed.

*Keywords:* Formazanes; 1:2 metal-complex dyes; Iron–dye complexes; Dyeing of wool and polyamide fibres

## 1. Introduction

Over the recent decade there has been a growing interest in so-called ecologically friendly dyes. This has been partially the result of reports concerned with potentially harmful interaction of clothing to human health due to the presence of various chemicals including dyes. In Europe many manufactures of textile garments try to meet the requirements of the Öko-Text Standard 100 which specifies the parameters and limits connected with ecologically safe textiles. In the case of garments dyed with metal-complexed dyes the most important factor is the amount of harmful metals which can be extracted with artificial saliva or perspiration solutions during corresponding fastness tests. From this point of view iron-complexed dyes may be considered as environmentally safe in view of the very low limits acceptable for chromium and cobalt-complexed dyes [1].

In the past, iron-complexed dyes were mainly used in the coloration of leather, and, as is apparent from reviews of the patent literature, this tendency still exists. One of the best known dyes of this type is C.I. Acid Brown 98 (Fig. 1) based on 1-(4′-sulfo)-phenyl-3-methyl-5-pyrazolone.

In this group disazo and trisazo dyes are also very popular based on the use of resorcinol as bis-coupling or tris-coupling component [2–5].

Iron complexes of monoazo dyes type 1:2 with good affinity for wool and polyamide fibres, have also been described. This group is prepared by the method typical for other metal-complexed dyes, i.e. coupling of diazotized *o*-amino-phenols or *o*-aminonaphthols with various coupling components followed by reaction with $Fe_{II}$ or $Fe_{III}$ salts in medium acidic to weakly alkaline environment.

The main disadvantage in application of iron complexes of azo dyes in dyeing wool and polyamide fibres is their colour range, which despite the use of various coupling components such as 1-naphthols [6,7], 2-naphthols [8,9], arylides of

---

* Corresponding author. Fax +48-42-636-25-96.

0143-7208/99/$ - see front matter
PII: S0143-7208(99)00033-9

acetoacetic acids [10], allows only yellow–brown to olive–brown, violet–brown and black–brown shades to be obtained. The same colouristic results were obtained during application of C.I. Mordant Dyes aftertreated on the wool fibre with iron salts [11].

Recently, more promising was the use of 1:2 iron complexes of 1,3,5-triarylformazanes of the structure presented in Fig. 2. In this case violet, blue and bluish-black dyeings exhibiting good lightfastness on dyed wool and polyamide fibres [12,13] were obtained. The latter group of dyes were synthesed by classical multistep reactions, involving preparation of the arylhydrazine, its condensation with benzaldehyde, coupling of the intermediate phenylhydrazone in aq. pyridine solution with the appropriate diazonium salt, and final conversion of the formazan dye to its metal complex [14].

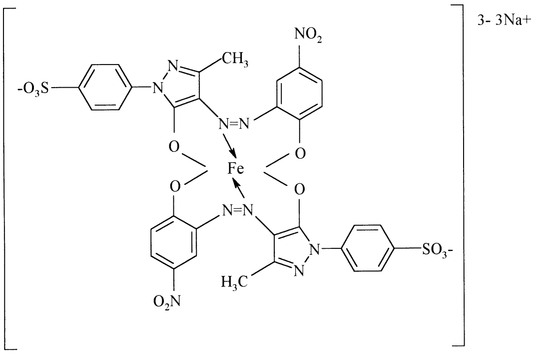


Fig. 1. C.I. acid brown 98.

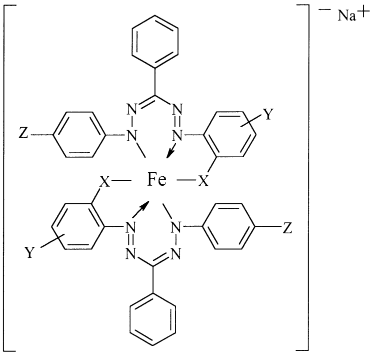


Fig. 2. Chemical structure of 1:2 Fe complexes of 1,3,5-triarylformazanes.

The purpose of this present work was the synthesis and determination of the fastness properties of 1:2 iron complexes of other formazanes, which were derivatives of 1,5-diaryl-3-cyanoformazane. These products can be obtained in a simple "one pot" reaction [14–16] as shown in Fig. 3 for some cases.

## 2. Results and discussion

### 2.1. Preparation of dyes and intermediates

The 1,5-diaryl-3-cyanoformazane dyes prepared during this work were synthesed in almost quantitative yield by coupling of ethyl cyanoacetate with diazotized derivatives of aniline in a weakly acidic environment (pH = 3.6–4.0). Hydrazones **1a**–**1c**, after alkaline hydrolysis of the carboxyethyl group, were then coupled in a strongly alkaline environment (pH = 10.0–13.0) with diazotized *o*-aminophenols or *o*-aminonaphthols to give with 70–90% yield of the formazanes of structures **2a**–**2j** and **3a**–**3f**. Iron complexes of these formazanes were also prepared in very good yield in aqueous solution at room temperature. The same results for the metalisation process were obtained in the pH range 5.0–8.0 and with the use of $Fe^{2+}$ or $Fe^{3+}$ salts. Finally 16

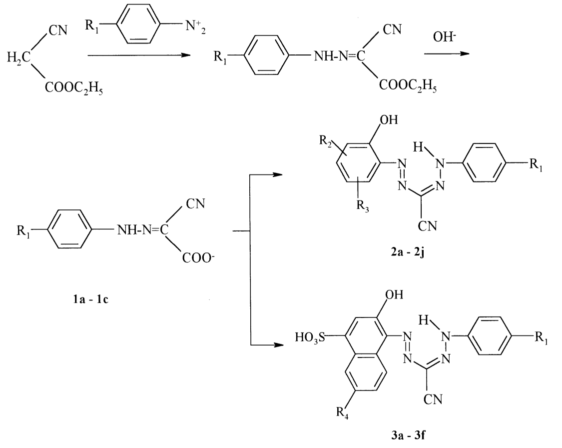


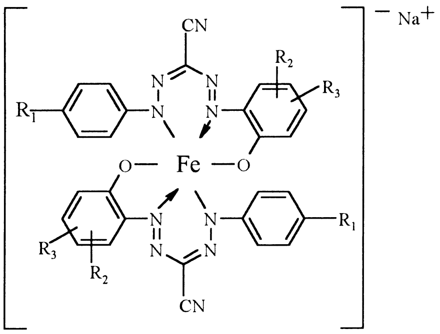
Fig. 3. Synthesis of 1,5-diaryl-3-cyanoformazanes **2a**–**2j** and **3a**–**3f**.

dyes, 1:2 iron complexes of 1,5-diaryl-3-cyanoformazane of the structures **4a–4j** and **5a– 5f** presented in Fig. 4 and in Table 1, were obtained.

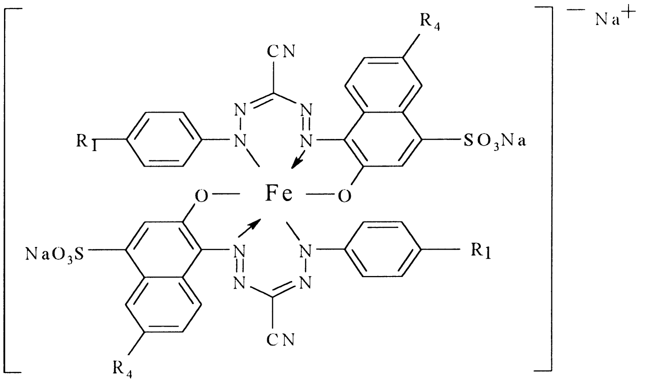
### *2.2. Absorption spectra of formazanes and their 1:2 Fe complexes*

All prepared formazanes and their 1:2 Fe complexes were characterised by their electronic absorption spectra in the visible region. It was found that the spectra of the formazanes changed due to their ionisation, depending on the pH values of the measured solutions. These changes differed for various formazanes depending on their chemical structure. To eliminate this phenomenon, a 50% ethanol–1% acetic acid mixture was used as solvent; in this medium none of the formazanes were more ionised. Absorption spectra of the 1:2 Fe complexes of formazanes were measured in 50% ethanol. Results of these measurements are listed in Table 2.

As can be seen from the data, the introduction of an iron atom into formazane molecule results in



**4a - 4j**



**5a - 5f**

Fig. 4. Chemical structure of 1:2 Fe complexes of dyes **4a–4j** and **5a–5f**.

Table 1
Chemical structure of 1:2 Fe complexes of dyes **4a–4j** and **5a–5f**

| No. | Dye | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|---|
| 1 | **4a** | $-SO_2NH_2$ | $4-NO_2$ | -H | – |
| 2 | **4b** | $-SO_2NH_2$ | $5-NO_2$ | -H | – |
| 3 | **4c** | $-SO_2NH_2$ | $4-SO_3H$ | -H | – |
| 4 | **4d** | $-SO_2NH_2$ | 4-Cl | -H | – |
| 5 | **4e** | $-SO_2NH_2$ | $4-SO_2NH_2$ | -H | – |
| 6 | **4f** | $-SO_2NH_2$ | $4-SO_2NH_2$ | $6-NO_2$ | – |
| 7 | **4g** | $-SO_2NH_2$ | 4-Cl | $5-SO_2NH_2$ | – |
| 8 | **4h** | $-SO_2NH_2$ | $4-SO_3H$ | $6-NO_2$ | – |
| 9 | **4i** | -H | $4-NO_2$ | -H | – |
| 10 | **4j** | -H | $5-NO_2$ | -H | – |
| 11 | **5a** | $-SO_2NH_2$ | – | – | -H |
| 12 | **5b** | $-SO_2NH_2$ | – | – | $-NO_2$ |
| 13 | **5c** | $-SO_3H$ | – | – | -H |
| 14 | **5d** | $-SO_3H$ | – | – | $-NO_2$ |
| 15 | **5e** | -H | – | – | -H |
| 16 | **5f** | -H | – | – | $-NO_2$ |

Table 2
Spectral properties of formazanes **2a–2j** and **3a–3f** and 1:2 Fe complexes of dyes **4a–4j** and **5a–5f**

| No. | Formazane | $\lambda_{max}$ (nm) | $\varepsilon_{mol}$ $10^{-4}$ | Dye | $\lambda_{max}$ (nm) | $\varepsilon_{mol}$ $10^{-4}$ |
|---|---|---|---|---|---|---|
| 1 | **2a** | 453 | 1.74 | **4a** | 512 | 3.14 |
| 2 | **2b** | 454 | 2.09 | **4b** | 538 | 1.54 |
| 3 | **2c** | 458 | 2.34 | **4c** | 534 | 1.99 |
| 4 | **2d** | 461 | 2.18 | **4d** | 539 | 1.90 |
| 5 | **2e** | 453 | 1.59 | **4e** | 517 | 2.45 |
| 6 | **2f** | 459 | 1.83 | **4f** | 493 | 1.89 |
| 7 | **2g** | 465 | 1.67 | **4g** | 536 | 1.89 |
| 8 | **2h** | 452 | 1.97 | **4h** | 485 | 2.19 |
| 9 | **2i** | 455 | 1.72 | **4i** | 483 | 2.22 |
| 10 | **2j** | 463 | 1.41 | **4j** | 517 | 1.17 |
| 11 | **3a** | 509 | 2.40 | **5a** | 577 | 2.37 |
| 12 | **3b** | 497 | 2.61 | **5b** | 559 | 3.04 |
| 13 | **3c** | 509 | 2.62 | **5c** | 572 | 2.54 |
| 14 | **3d** | 495 | 2.82 | **5d** | 559 | 2.69 |
| 15 | **3e** | 506 | 2.48 | **5e** | 568 | 2.31 |
| 16 | **3f** | 480 | 1.96 | **5f** | 552 | 2.84 |

a strong bathochromic shift, usually in the order of 60–80 nm. The influence of substituents with strong electronegative activity located in the phenylene ring in positions 2 and 4 (dyes **4f** and **4h**) decreases this shift to 30 nm. The observed bathochromic shift is usually accompanied by a broadening of the absorption curve, as shown in Fig. 5. In some cases, increase of the molar absorption coefficient of the final dye was also observed.

As was expected, the change from *o*-aminophenols to *o*-aminonaphthols in the dye molecule gave products which absorbed at longer wavelengths, and usually exhibited higher molar absorption values.

### *2.3. Application and fastness properties of iron-complexed dyes*

All the prepared 1:2 Fe complexes of 1,5-diaryl-3-cyanoformazanes were used to dye wool and polyamide fibres. It is apparent from the data presented in Table 3 that the dyeing of wool fabric at a 1% dye concentration resulted in a series of brown, violet, blue and navy blue colours. The dyes exhibited almost quantitative dyebath exhaustion except for dyes **4c**, **5c** and **5d**, in which the presence of additional sulphonic groups decreased the affinity of the dye to the fibre. All dyeings had very good

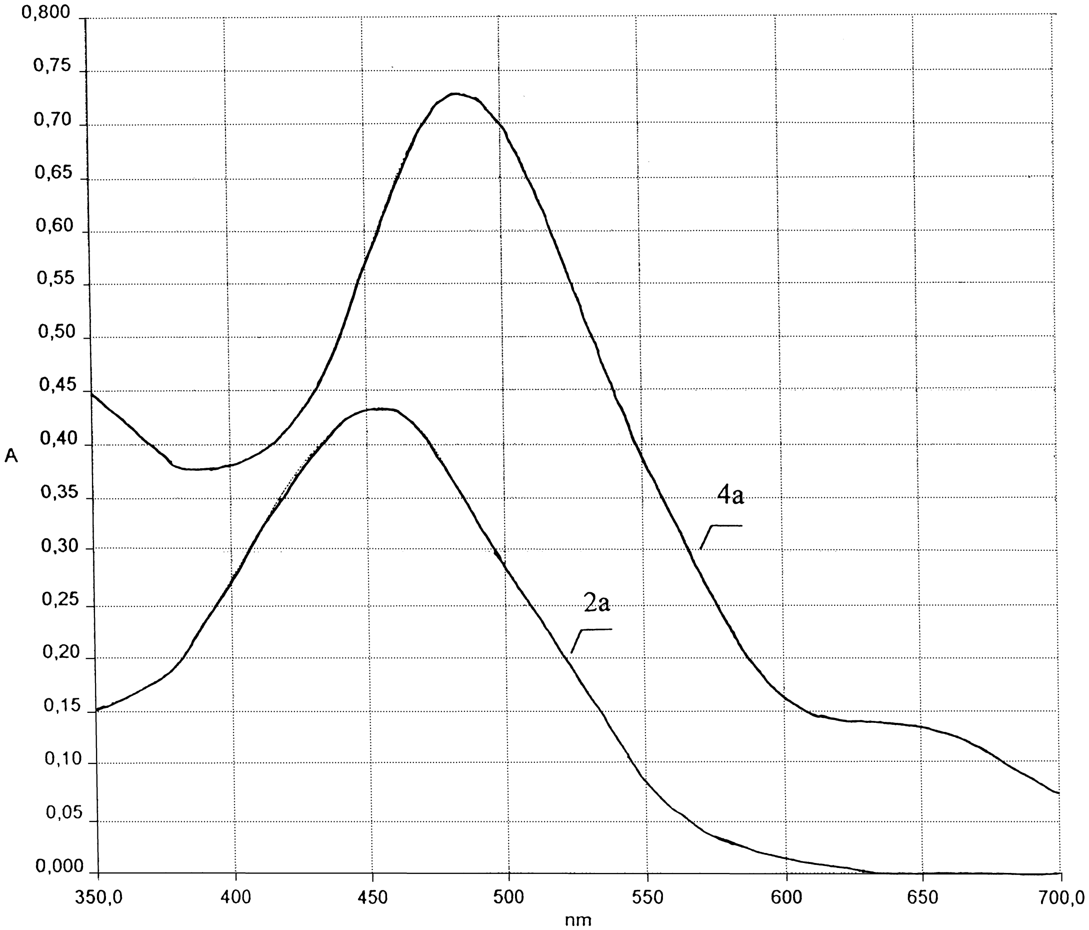


Fig. 5. Absorption spectra of formazane **2a** and 1:2 Fe complex of dye **4a** (1 cm path length, conc. $2.5\times10^{-5}$ mol dm$^{-3}$).

Table 3
Fastness properties of 1:2 Fe complexes of formazane dyes **4a**–**4j** and **5a**–**5f** on wool fibre (1% dyeings)

| No. | Dye | Colour on wool fabric | Exhaustion from dyebath | Wash fastness (40°C)[a] | | Acid perspiration[a] | | Wet rubbing[a] | Lightfastness[b] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Colour change | Staining of cotton | Colour change | Staining of wool | | |
| 1 | **4a** | Red brown | 100.0 | 5- | 4–5 | 5 | 4–5 | 5 | 6 |
| 2 | **4b** | Dark violet | 99.3 | 5 | 5 | 5 | 4–5 | 4–5 | 5 |
| 3 | **4c** | Violet | 56.6 | 5 | 4–5 | 5 | 5 | 4–5 | 4–5 |
| 4 | **4d** | Dark violet | 100.0 | 4 | 3 | 4–5 | 5 | 4–5 | 5 |
| 5 | **4e** | Brown violet | 98.8 | 5 | 5 | 5 | 5 | 5 | 6 |
| 6 | **4f** | Brown | 99.5 | 5 | 5 | 5 | 4–5 | 5 | 7 |
| 7 | **4g** | Violet | 100.0 | 5 | 5 | 5 | 4–5 | 5 | 4–5 |
| 8 | **4h** | Brown | 98.3 | 5 | 5 | 5 | 5 | 4–5 | 6 |
| 9 | **4i** | Brown | 100.0 | 4–5 | 5 | 5 | 5 | 4 | 6 |
| 10 | **4j** | Brown | 98.6 | 5 | 5 | 5 | 5 | 4–5 | 6 |
| 11 | **5a** | Blue | 96.1 | 4–5 | 5 | 5 | 5 | 5 | 5 |
| 12 | **5a***[c] | Navy blue | 94.1 | 5 | 5 | 5 | 5 | 4–5 | 5 |
| 13 | **5b** | Violet brown | 100.0 | 5 | 5 | 5 | 5 | 5 | 6 |
| 14 | **5b**** | Black | 96.5 | 5 | 5 | 4–5 | 4–5 | 5 | 5 |
| 15 | **5c** | Blue | 70.6 | 3–4 | 4–5 | 5 | 5 | 4–5 | 4 |
| 16 | **5d** | Violet | 66.1 | 4–5 | 5 | 5 | 4–5 | 4–5 | 4 |
| 17 | **5e** | Navy blue | 99.7 | 5 | 5 | 5 | 5 | 4–5 | 4–5 |
| 18 | **5e**** | Navy blue | 81.0 | 4–5 | 5 | 5- | 4–5 | 4–5 | 4–5 |
| 19 | **5f** | Violet | 94.7 | 4–5 | 5 | 5 | 5 | 5 | 6 |
| 20 | 4a + 5a*** | Brown black | 96.0 | 5 | 5 | 4–5 | 5 | 4–5 | 5 |

[a] In 5-grade scale: 1-the lowest, 5-the highest.
[b] In 8-grade scale: 1 = the lowest, 8 = the highest.
[c] *2% dyeings, **3% dyeings, ***3% dyeings of the mixture **4a** and **5a** (1:3).

fastness in washing, alkaline perspiration and wet rubbing; lightfastness of the dyeings varied from fairly good to very good, and was excellent in the case of dye **4f**.

The results of the dyeings of polyamide fibre were even better, as can be seen from the data in Table 4. At 1% concentration of dye in the dyebath, all dyes, except the above mentioned dyes **4c**, **5c** and **5d**, exhibited almost quantitative exhaustion on the fibre, and gave the same colour range. Increase of the dye concentration in the dyebath to 2 and 3%, gave, in the case of dyes **5b**, **5e** and **5f**, interesting black dyeings with good light and wetfastness. Similar results were obtained during 3% dyeing of polyamide fibre with a mixture of dyes **4a** and **5b** (1:3). Moreover, at higher dyebath concentrations all the latter mentioned dyes build up well on polyamide fibre showing a very high exhaustion ratio (above 95%). All these properties thus allow them to be considered as potentially viable from a practical viewpoint.

## 3. Experimental

### 3.1. *Synthesis of dyes and intermediates*

The synthesis of hydrazones, formazanes and final dyes were carried out with the use of commercial intermediates without their further purification.

#### 3.1.1. *Preparation of hydrazone **1b***

3.42 g (0.02 mole) 4-aminobenzenesulfonamide was dissolved in 50 cm$^3$ water and 5 cm$^3$ 30%HCl. After cooling with ice to 0–5°C, diazotisation was effected by the addition of 5 cm$^3$ 4*N* $NaNO_2$ (diazotisation time 30 min). Over the next 30 min, the diazonium liquor was added to a mixture of 2.5 g (0.022 mole) of ethyl cyanoacetate in 20 cm$^3$ of water at 20–25°C. During this time, the pH of the reaction mixture was maintained at 3.6–4.0 by addition of a saturated solution of sodium acetate. The reaction mixture was stirred without additional cooling for a further 1–2 h until coupling was completed. The reaction mixture was then made alkaline by addition of 11.2 g KOH dissolved in 50 cm$^3$ of water, heated to 80°C, and kept at this temperature for 30 min. After completing the hydrolysis of the carboxyethyl group (monitoring by TLC, see Table 5) the reaction mixture was cooled to below 10°C, and with the use of 30% HCl, acidified to pH 2.5–3.5. During this stage the temperature of the mixture was kept

Table 4
Fastness properties of 1:2 Fe complexes of formazane dyes **4a**–**4j** and **5a**–**5f** on polyamide fibre (1% dyeings)

| No. | Dye | Colour on polyamide fabric | Exhaustion from dyebath | Wash fastness (40°C)[a] | | Acid prespiration[a] | | Wet rubbing[a] | Lightfastness[b] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Colour change | Staining of cotton | Colour change | Staining of wool | | |
| 1 | **4a** | Red brown | 100.0 | 5 | 5 | 5 | 5– | 5 | 5–6 |
| 2 | **4b** | Dark violet | 100.0 | 5 | 5 | 5 | 5– | 5 | 5–6 |
| 3 | **4c** | Violet | 37.4 | 5 | 4–5 | 5 | 5 | 5 | 4 |
| 4 | **4d** | Dark violet | 100.0 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | **4e** | Red violet | 100.0 | 5 | 5 | 5 | 5 | 5 | 4 |
| 6 | **4f** | Brown | 100.0 | 5 | 5 | 5 | 5 | 4–5 | 6 |
| 7 | **4g** | Violet | 100.0 | 5 | 5 | 5 | 4–5 | 5 | 5 |
| 8 | **4h** | Brown | 100.0 | 5 | 5 | 5 | 5 | 4–5 | 4 |
| 9 | **4i** | Brown | 100.0 | 5 | 5 | 5 | 4–5 | 4–5 | 6 |
| 10 | **4j** | Violet brown | 100.0 | 5 | 5 | 5 | 5 | 4–5 | 6–7 |
| 11 | **5a** | Blue | 98.5 | 4–5 | 5 | 5 | 5 | 4–5 | 4 |
| 12 | **5a***[c] | Navy blue | 97.3 | 5 | 5 | 5 | 5 | 5 | 4–5 |
| 13 | **5b** | Violet | 100.0 | 5 | 5 | 5 | 5 | 5 | 5 |
| 14 | **5b**** | Black | 98.1 | 5 | 5 | 5 | 5 | 5 | 5 |
| 15 | **5c** | Blue | 47.4 | 5 | 4–5 | 5 | 3–4 | 5 | 3 |
| 16 | **5d** | Voilet | 91.4 | 5 | 5 | 5 | 5 | 5 | 4 |
| 17 | **5e** | Navy blue | 99.5 | 5 | 5 | 5 | 5– | 4 | 4–5 |
| 18 | **5e**** | Black | 97.1 | 5– | 5 | 5 | 5 | 4–5 | 5 |
| 19 | **5f** | Violet brown | 100.0 | 5 | 5 | 5 | 5 | 4–5 | 6 |
| 20 | **5f**** | Black | 98.1 | 4–5 | 5 | 5– | 5 | 4–5 | 7 |
| 21 | **4a + 5a***** | Black | 97.0 | 5 | 5 | 5 | 5 | 4–5 | 5 |

[a] In 5-grade scale: 1 = the lowest, 5 = the highest.
[b] In 8-grade scale: 1 = the lowest, 8 = the highest.
[c] 2% dyeings, **3% dyeings, ***3% dyeings of the mixture **4a** and **5a** (1:3).

Table 5
Physicochemical properties of hydrazones **1a**–**1c**

| No. | Hydrazone | $R_1$ | Yield (%) | *Rf*[a] | m.p. (*°C) | $^1$H NMR $\delta$ (ppm), (J) (Hz)[b] | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Ar-H | -COOH | Others |
| 1 | **1a** | -H | 97 | 0.32 | 154–6 | T; 1H; 7,12 (8.0)<br>T; 2H; 7.34 (8.0)<br>D; 2H; 7.46 (8.0) | S; 1H; 12.5 | – |
| 2 | **1b** | -SO$_2$*NH$_2$* | 95 | 0.18 | 162–3 | D; 2H; 7.60 (8.75)<br>D; 2H; 7.82 (8.75) | S; 1H; 12.25 | S; 2H; 7.30 |
| 3 | ***1c*** | -SO$_3$H | 94 | 0.10 | –<br>– | D; 2H; 7.65 (8.5)<br>D; 2H; 7.87 (8.5) | S; 1H; 12.25 | S; 1H; 10.80<br>0 |

[a] On Silica gel 60-Merck plates, eluent buthanol. [b]DMSO used as the solvent.

Table 6
*Rf* and $^1$H NMR data of formazanes **2a**–**2j** and **3a**–**3f**

| No. | Formazane | *Rf* | $^1$H NMR $\delta$ (ppm) (J) (Hz)$^c$ | | |
|---|---|---|---|---|---|
| | | | Ar–H for phenol or naphtol | Others Ar–H | Others |
| 1 | **2a** | 0.80$^a$ | d, 1H, 7.02 (9.0); dd, 1H, 7.91 (9.0, 2.8); d, 1H, 8.41 (2.8) | d, 2H, 7.63 (8.5); d, 2H, 7.80 (8.5) | s, 2H, 7.27 (-$SO_2NH_2$) |
| 2 | **2b** | 0.92$^a$ | d, 1H, 7.48 (9.0); dd, 1H, 7.72 (9.0, 2.5); d, 1H, 8.01 (2.5) | d, 2H, 7.66 (8.5); d, 2H, 7.82 (8.5) | s, 2H, 7.29 (-$SO_2NH_2$) |
| 3 | **2c** | 0.47$^b$ | d, 1H, 7.04 (8.5); dd, 1H, 7.73 (8.5, 2.3); d, 1H, 8.01 (2.3) | d, 2H, 7.67 (8.5); d, 2H, 7.85 (8.5) | s, 2H, 7.30 (-$SO_2NH_2$)<br>s, 1H, 10.70 (-$SO_3H$) |
| 4 | **2d** | 0.93$^a$ | d, 1H, 6.02 (8.5); dd, 1H, 7.60 (8.5, 2.3); d, 1H, 7.95 (2.3) | d, 2H, 7.62 (8.5); d, 2H, 7.81 (8.5) | s, 2H, 7.31 (-$SO_2NH_2$) |
| 5 | **2e** | 0.87$^a$ | d, 1H, 6.93 (8.5); dd, 1H, 7.40 (8.5, 2.3); d, 1H, 7.84 (2.3) | d, 2H, 7.56 (8.7); d, 2H, 7.76 (8.7) | s, 2H, 7.16 (-$SO_2NH_2$)<br>s, 2H, 7.23 (-$SO_2NH_2$) |
| 6 | **2f** | 0.45$^a$ | s, 1H, 8.05; s, 1H, 8.11 | d, 2H, 7.84 (8.5); d, 2H, 7.92 (8.5) | s, 2H, 7.16 (-$SO_2NH_2$)<br>s, 2H, 7.43 (-$SO_2NH_2$) |
| 7 | **2g** | 0.83$^a$ | s, 1H, 7.40; s, 1H, 7.74 | d, 2H, 7.63 (8.5); d, 2H, 7, 80 (8.5) | s, 2H, 7.27 (-$SO_2NH_2$)<br>s, 2H, 7.46 (-$SO_2NH_2$) |
| 8 | 2h | 0.08$^b$ | s, 1H, 8.39; s, 1H, 8.64 | d, 2H, 7.76 (8.0); d, 2H, 7.86 (8.0) | s, 2H, 7.34 (-$SO_2NH_2$)<br>s, 1H, 11.74 (-$SO_3H$) |
| 9 | **2i** | 0.93$^a$ | d, 1H, 7.80 (9.0); dd, 1H, 7.79 (8.0, 3.0); d, 1H, 8.09 (3.0) | t, 1H, 7.17 (8.0); t, 2H, 7.38 (8.0); d, 2H, 7.54 (8.0) | – |
| 10 | **2j** | 0.91$^a$ | d, 1H, 7.14 (8.8); d, 1H, 7.53 (2.5); dd, 1H, 7.71 (8.8, 2.5) | t, 1H, 7.31 (7.5); t, 2H, 7.41 (7.5); d, 2H, 7.57 (7.5) | – |
| 11 | 3a | 0.50$^b$ | t, 1H, 7.53 (8.5); s, 1H, 7.67; t, 1H, 7.69 (8.5); d, 1H, 8.69 (8.5); d, 1H, 8.82 (8.5) | d, 2H, 7.62 (8.0); d, 2H, 7.86 (8.0) | s, 2H, 7.29 (-$SO_2NH_2$)<br>s, 1H, 11.74 (-$SO_3H$) |
| 12 | **2b** | 0.62$^b$ | s, 1H, 7.75; d, 1H, 8.45 (8.5); d, 1H, 8.84 (8.5); s, 1H, 9.69 | d, 2H, 7.68 (8.0); d, 2H, 7.89 (8.0) | s, 2H, 7.29 (-$SO_2NH_2$)<br>s, 1H, 12.82 (-$SO_3H$) |
| 13 | **3c** | 0.19$^b$ | t, 1H, 7.46 (8.5); t, 1H, 7.61 (8.5); s, 1H, 7.65; d, 1H, 8.69 (8.5); d, 1H, 8.80 (8.5) | d, 2H, 7.52 (8.0); d, 2H, 7.68 (8.0) | s, 1H, 11.61 (-$SO_3H$)<br>s, 1H, 12.88 (-$SO_3H$) |
| 14 | **3d** | 0.16$^b$ | s, 1H, 7.80; d, 1H, 8.42 (9.0); d, 1H, 8.81 (9.0); s, 1H, 9.76 | d, 2H, 7.50 (8.0); d, 2H, 7.71 (8.0) | s, 1H, 11.78 (-$SO_3H$)<br>s, 1H, 12.98 (-$SO_3H$) |
| 15 | **3e** | 0.66$^b$ | t, 1H, 7.37 (9.0); t, 1H, 7.63 (9.0); s, 1H, 7.67; d, 1H, 8.69 (9.0); d, 1H, 8.80 (9.0) | t, 1H, 7.19 (8.0); t, 2H, 7.42 (8.0); d, 2H, 7.52 (8.0) | s, 1H, 11, 64 (-$SO_3H$) |
| 16 | **3f** | 0.73$^b$ | s, 1H, 7.59; d, 1H, 8.02 (9.0); d, 1H, 8.46 (9.0); s, 1H, 9.11 | t, 1H, 7.17 (7.5); t, 2H, 7.27 (7.5); d, 2H, 7.34 (7.5) | s, 1H, 12, 90 (-$SO_3H$) |

[a] On Aluminiumoxid 150 F254 neutral (Typ T) plates, eluent: *n*-buthanol: water: acetic acid, 8:1:1.

[b] On Silica gel 60 Merck plates; eluent *n*-buthanol.

[c] $^1$H NMR **2a**–**2j** and **3a**–**3e** in DMSO; $^1$H NMR **3f** in $D_2O$ as the solvent.

below 20°C. The precipitate which separated was filtered off and washed with 20 cm$^3$ of distilled water. After drying, 5.2 g (97% theoretical yield) of the hydrazone **1b** was obtained. The structure of this product was confirmed by $^1$H NMR (see Table 5).

Physicochemical and analytical data of hydrazone **1b**, and of hydrazones **1a** and **1c** prepared in a similar way, are presented in Table 5.

### 3.1.2. *Preparation of formazane **2a***

3.08 g (0.02 mole) of 2-amino-4-nitrophenol was dissolved in 50 cm$^3$ water and 5 cm$^3$ 30% HCl. After cooling with ice to 0–5°C, it was diazotized by the addition of 5 cm$^3$ 4*N* $NaNO_2$; diazotisation time 30 min, temperature below 5°C. During the next 30 min, the diazonium liquor was added in portions to 5.36 g (0.02 mole) of hydrazone **1b** dissolved in 50 cm$^3$ water and 2 cm$^3$ 30% aq. NaOH. The reaction mixture was stirred without additional cooling for a further 2–3 h until coupling was completed (test of the sample on filter paper with a solution of resorcinol for the presence of unreacted diazonium salt). The formazane dye **2a** was separated by acidifying the reaction mixture to pH about 8.0 with the use of dilute hydrochloric acid, and salting out (20% vol) with sodium chloride. The product was filtered and washed with 50 cm$^3$ of 20% aq. NaCl. After drying, 10.4 g of a dark coloured powder, with 77.8% content of formazane **2a** (96% theoretical yield), was obtained.

The same method was used in the case of formazanes **2b**–**2j**; their physico-chemical and analytical data are presented in Table 6.

### 3.1.3. *Preparation of formazane **3a***

5.0 g (0.02 mole) of 1-diazo-2-naphthol-4-sulphonic acid (8.33 g technical product of 60% purity) was dispersed in 30 cm$^3$ of water. After cooling with ice to 0–5°C, 30% NaOH solution was added gave pH = 7.0 (±0.2). The diazonium salt was then added at room temperature to 5.36 g (0.02 mole) of hydrazone **1b** dissolved in 50 cm$^3$ water and 2 cm$^3$ 30% aq. NaOH. The reaction mixture was stirred without additional cooling for a further 3 h. During this time, the pH of the reaction mixture was maintained at 10–13 by addition of 30% aq. NaOH. The formazane dye **3a** was separated by acidifying the reaction mixture to about 8.0 with dilute hydrochloric acid and salting out (25% vol) with sodium chloride. The product was filtered and washed with 100 cm$^3$ of 25% aq. NaCl. After drying, 15.6 g of a dark coloured powder, with 70.7% content of formazane **3a** (90% theoretical yield), was obtained.

Table 7
*Rf* and FAB analysis data of dyes **4a**–**4j** and **5a**–**5f**

| No. | Dye | *Rf* | FAB | | |
|---|---|---|---|---|---|
| | | | Assignment[c] | *m*/*z* | Relative abundance |
| 1 | **4a** | 0.69[a] | $[M]^-$ | 853 | 16.29 |
| | | | $[M–Na]^-$ | 830 | 45.46 |
| 2 | **4b** | 0.81[a] | $[M]^-$ | 853 | 15.68 |
| | | | $[M–Na]^-$ | 830 | 72.30 |
| 3 | **4c** | 0.21[b] | $[M–H]^-$ | 922 | 9.14 |
| | | | $[M–Na]^-$ | 900 | 32.53 |
| 4 | **4d** | 0.81[a] | $[M]^-$ | 798 | 12.25 |
| | | | $[M–Na]^-$ | 775 | 51.83 |
| 5 | **43** | 0.70[a] | $[M]^-$ | 921 | 18.77 |
| | | | $[M–Na]^-$ | 898 | 61.48 |
| 6 | **4f** | 0.34[a] | $[M]^-$ | 1011 | 14.71 |
| | | | $[M–Na]^-$ | 988 | 44.29 |
| 7 | **4g** | 0.59[a] | $[M]^-$ | 991 | 8.45 |
| | | | $[M–Na]^-$ | 968 | 39.82 |
| 8 | **4h** | 0.32[b] | $[M–H]^-$ | 1012 | 5.23 |
| | | | $[M–Na]^-$ | 990 | 51.94 |
| 9 | **4i** | 0.85[a] | $[M]^-$ | 695 | 19.23 |
| | | | $[M–Na]^-$ | 672 | 58.49 |
| 10 | **4j** | 0.80[a] | $[M]^-$ | 695 | 17.64 |
| | | | $[M–Na]^-$ | 672 | 61.02 |
| 11 | **5a** | 0.24[b] | $[M–H]^-$ | 1022 | 6.81 |
| | | | $[M–Na]^-$ | 1000 | 45.22 |
| 12 | **5b** | 0.35[b] | $[M–H]^-$ | 1111 | 7.55 |
| | | | $[M–Na]^-$ | 1090 | 40.89 |
| 13 | **5c** | 0.03[b] | $[M–H]^-$ | 1024 | 3.45 |
| | | | $[M–Na]^-$ | 1002 | 27.19 |
| 14 | **5d** | 0.07[b] | $[M–H]^-$ | 1114 | 4.95 |
| | | | $[M–Na]^-$ | 1092 | 26.81 |
| 15 | **5e** | 0.15[b] | $[M–H]^-$ | 864 | 7.78 |
| | | | $[M–Na]^-$ | 842 | 42.17 |
| 16 | **5f** | 0.23[b] | $[M–H]^-$ | 954 | 5.53 |
| | | | $[M-Na]^-$ | 932 | 35.87 |

[a] On Aluminiumoxid 150 F254 neutral (Type T) plates (Merck); eluent: *n*-buthanol: water: acetic acid, 8:1:1.

[b] On Silica gel 60 (Merck) plates; eluent *n*-buthanol.

[c] Ion abundance are expressed relative to the base peak *m*/*z* = 153 (3-nitrobenzyl alcohol as the matrix).

The same method was used in the case of formazanes **3b–3f**; their physicochemical and analytical data are presented in Table 6.

### 3.1.4. Preparation of Dye *4a*

7.8 g (0.02 mole) of formazane **2a** was dissolved at 25°C in 100 $cm^3$ water and 2 $cm^3$ 30% aq. NaOH. A solution of 1.3 g $FeSO_4$ $7H_2O$ in 10 $cm^3$ of water was added and the reaction mixture was stirred at pH 6–7 for 1 h until the process was completed (TLC analysis, Merck Aluminiumoxid 150 F 254 type T plates; water, acetic acid, *n*-buthanol = 1:1:8 as eluent). The dye was precipitated by addition of 10 g NaCl (approx. 10% vol), filtered and washed with 50 $cm^3$ 20% aq. NaCl. After drying, 10.7 g of a dark coloured powder, dye **4a** was obtained.

The same method was used in the case of other dyes, except **4h–4j**, which were separated by evaporation of the reaction mixture. Structures of the dyes were confirmed by FAB mass spectroscopy. Analytical data of all dyes are presented in Table 7.

### 3.2. Characterisation of products

All melting points are uncorrected. Visible spectra were recorded on a Perkin–Elmer Lambda 40 UV–VIS spectrophotometer. Absorption spectra of the formazanes were measured in a 50% ethanol–1% acetic acid mixture. Absorption spectra of the 1:2 Fe complexes of formazanes were measured in 50% ethanol. All formazanes and their Fe complexes were previously recrystalized from ethanol. $^1H$ NMR spectra were recorded on a Brucker DPX 250 spectrometer in DMSO solution. FAB mass spectra were recorded on a Finningam Mat MAT 94 (Switzerland) spectrometer in a 3-nitro-benzyl alcohol matrix.

### 3.3. Application and fastness tests

The dyeing of wool and polyamide fabric was carried out on a Rotec (Roaches, U.K.) laboratory dyeing machine by a dyeing process typical for acid dyes at dyebath pH 4.0 (acetic acid). Dyebath exhaustion were measured with the use of a Perkin–Elmer Lambda 40 UV–VIS spectrophotometer by the usually applied method [17]. Lightfastness data were determined with the use of Heraeus Xenotest 150 s. Lightfastness and other fastness tests were carried out according to the methods recommended by Polish Standards, which correspond with British and ISO Standards [18].

## Acknowledgements

The presented work was sponsored by the Polish Committee of Scientific Research, Project No. 3 T09B 08512.

## References

[1] Sewekow U. Textile Chemist and Colorist 1996;28:21–7.
[2] Ciba-Geigy, European Patent 423071, 1991.
[3] BASF. German Patent 4126995, 1991.
[4] Sandoz. German Patents 4133166 and 4133167, 1992.
[5] Boruta SA. Polish Patents 159369 and 159388, 1992.
[6] Sokolowska-Gajda J, Freeman HS, Reife A. Textile Res. Journal 1994;64:388.
[7] Freeman HS, Sokolowska-Gajda J, Reife A. US patent 5376151, 1994.
[8] Blus K. Przegl. Wlok. 1996;70:19 (in Polish).
[9] Czajkowski W, Blus K, Sokolowska-Gajda J, Szymczyk M, Wojciechowska A. Pol. patent application P-311606, 1995.
[10] Czajkowski W, Blus K, Sokolowska-Gajda J, Stolarski R, Szymczyk M. Polish patent application P-310453, 1995.
[11] Czajkowski W, Szymczyk M. Dyes and Pigments 1998;37:197–204.
[12] Sokolowska-Gajda J, Freeman HS, Reife A. Dyes and Pigments 1996;30:1–20.
[13] Freeman HS, Sokolowska-Gajda J, Reife A. US patent 5677434, 1996.
[14] Venkataraman K. The chemistry of synthetic dyes, vol. 3. New York/London: Academic Press, 1970. p. 373.
[15] Vesely M, Muzik F, Poskocil J. Coll Czech Chem Comm 1961;26:2530–41.
[16] Czajkowski W, Sokolowska-Gajda J, Stolarski R, Szymczyk M. Polish patent applications P-325446 and P-325629, 1998.
[17] Burkinshaw SM, Skelton H. Dyes and Pigments 1994;26:15–32.
[18] Society of Dyes and Colourists. Standard methods for the determination of the colour fastness of textiles and leather. Bradford: Society of Dyes and Colourists, 1978.