

A ONE-POT SYNTHESIS OF SOME NOVEL TETRAKISAZO DISPERSE DYES BEARING TWENTY-MEMBERED MACROCYCLIC POLY(AZOMETHINE)

Irma LAGVILAVA¹, Tea MATITAISHVILI², Ia IARDALASHVILI³ and Elizbar ELIZBARASHVILI^{4,*}

Division of Organic Chemistry, Department of Chemical Technology, Georgian Technical University, 77 Kostava Str., Tbilisi, 0175, Georgia; e-mail: ¹irma_lagvilava@gtu.ge, ²t_matitaishvili@yahoo.com, ³ia_iardalashvili@yahoo.com, ⁴elizbarashvili@gtu.ge

Received April 12, 2008

Accepted August 1, 2008

Published online February 28, 2009

Multiple-chromophore-containing dyes have been synthesized by azo coupling of twenty-membered poly(azomethine) dye **1** and 3-nitro- (**2a**) or 2,4-dinitrobenzene-1-diazonium tetrafluoroborate (**2b**) in solvents of various polarity (water, chloroform) in the presence or absence of dibenzo-18-crown-6 as phase transfer catalyst. The dyeing ability of the dyes was investigated as well as spectral and kinetic study of azo coupling was performed. The obtained disperse dyes are suitable for dyeing Nylon and polyester fibers from light reddish-brown to dark brown colors with good uniformity of dyeing as well as light, washing and sublimation fastness.

Keywords: Macrocycles; Disperse dyes; Azomethine; Phase transfer catalysis; Azo coupling; Hydrazones; UV-Vis spectroscopy.

In the recent decades, the interest in disperse dyes containing heterocycles has been grown as indicated by patent literature¹ and other publications². These dyes are commonly considered as environment-friendly products.

At present, azo dyes, in particular monoazo dyes, are one of the most frequent synthetic dyes used in various fields of industry and research³, due to their flexibility and low cost of the diazotization and azo coupling processes. The synthesis of bis-, tris- and in particular polyazo dyes is complicated or impossible. For this reason azo dyes are used for dyeing from yellow to blue colors in most cases. More deep hues are rare. Therefore, a combination of two or more different colors is used for obtaining deep hues. Hence, the synthesis of aromatic matrixes, capable of giving polyazo dyes, characterized by deep colors seems very interesting and significant.

Another important class of synthetic dyes is azomethines. These are well known luminescent dyes⁴. The interest in azomethine compounds has also been growing because of their antimicrobial, antituberculosis and anti-tumor activity⁵.

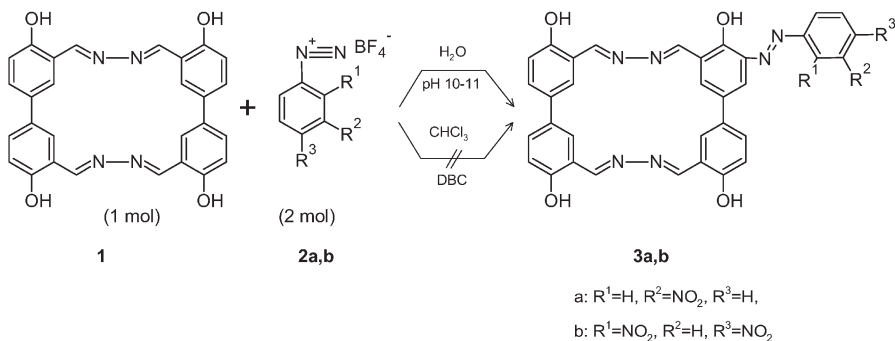
In a recent paper we have described the method of synthesis of twenty-membered macrocyclic azomethine compounds⁶. The poly(azomethine) dyes have a conjugated π -electron system and a "crown-like" hole. A few electrophilic substitution reactions have been run for the experimental establishment of aromaticity, stability and chemical reactivity of these twenty-membered macrocyclic azomethine dyes⁷.

In the present paper we undertake a detailed study of the azo coupling reaction of twenty-membered poly(azomethine) dye **1** and 3-nitro- (**2a**) and 2,4-dinitrobenzene-1-diazonium salts (**2b**) in the media of various polarity (water, chloroform). The performance of the dyes and spectral and kinetic study of the azo coupling reactions have been also investigated.

RESULTS AND DISCUSSION

Synthesis

The azo coupling of diazonium salts **2a** or **2b** and twenty-membered poly(azomethine) dye **1** has been carried out in polar media (aqueous solution of NaOH). Diazonium salts as tetrafluoroborates were prepared from corresponding primary aromatic amines, sodium nitrite and tetrafluoroboric acid, isolated and dried in air. The obtained diazonium salts **2a** and **2b** have been checked for reactivity (azo coupling with alkaline H acid solution) before each run of azo coupling.



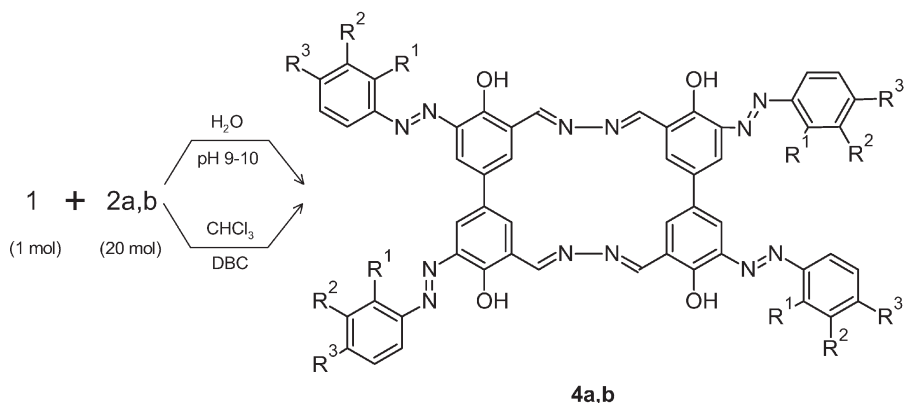
SCHEME 1

Azo coupling of **1** and **2a** or **2b** (molar ratio 1:2)

Azo coupling of **1** and **2a** (in molar ratio 1:2) was carried out by addition of water solution of a diazonium salt to an alkali solution of **1**. The coupling was usually accompanied by some decomposition; however, 58–59% yields of the main product **3a** was usually obtained. The spectral and elemental analysis of the dye showed that the main reaction product is monosubstituted azo derivative of **1**. Bis- and some polysubstituted azo derivatives are formed only in trace amount (Scheme 1).

2,4-Dinitrobenzene-1-diazonium tetrafluoroborate (**2b**) reacts with **1** in the same manner and gives the monosubstituted macrocyclic poly(azomethine) compound **3b** as a main product with the yield up to 64%.

In the synthesis of polyazo dyes, the azo coupling was carried out in the presence of a large excess of **2a** or **2b**. Poly(azomethine) **1** was treated with twenty-fold excess of **2a** or **2b**. The obtained dyes have been isolated and characterized as described above. The data shows that the main product of the azo coupling of **1** and **2a** or **2b** of the molar ratio 1:20 is a mixture of tetrasubstituted dyes **4a** and **4b** (Scheme 2). The final products **4a** and **4b** were isolated as reddish-brown and dark-brown solids in yields 58 and 61%, respectively.



SCHEME 2

Azo coupling of **1** and **2a** or **2b** (molar ratio 1:20)

A preponderance of literature on azo coupling reactions conducted in aqueous or polar organic solvents. Reports on azo coupling in non-polar media are still rare. In our previous paper, we have indicated that in some

cases diazonium cations are more reactive in non-polar, than in polar media and, therefore, it has been expedient to carry out the azo coupling reaction with low-active azo components in such solvents⁸.

Therefore, azo coupling of **1** and **2a** or **2b** has been carried out also in chloroform. The reactions have been run at various molar ratios (from 1:2 to 1:20) in the presence of dibenzo-18-crown-6 (DBC) as a phase transfer catalyst.

To our surprise, azo coupling was successful only with **2b**. 3-Nitrobenzene-1-diazonium tetrafluoroborate (**2a**) is unable to couple to **1** in chloroform in the presence of DBC, while 2,4-dinitrobenzene-1-diazonium tetrafluoroborate (**2b**) reacts with **1** and gives monosubstituted **1** in the 1:2 molar ratio with yields up to 64% and with tetrasubstituted **1** in the 1:20 molar ratio with yields up to 67%.

The reason for such behavior of diazonium salts is due to the reactivity of **1**. In aqueous alkali media, it reacts as a rather more reactive form of phenolate ion than the neutral phenolic form existing in chloroform. Another reason could be low electrophilicity of the 3-nitrobenzene-1-diazonium cation, compared with 2,4-dinitrobenzen-1-diazonium.

Spectral Properties

Absorption maxima of azo dyes **3a**, **3b**, **4a** and **4b** were recorded in ethanol solution. The resulting data are given in Experimental. As far as the absorption maxima are concerned, the λ_{\max} values are directly proportional to the electron properties of the substituents in the ring system. The values of the logarithm of molar absorption coefficient ($\log \epsilon$) of the dyes were in the range 5.18–5.37 consistent with their high absorption. The presence of electron-donating and electron-attracting groups at suitable positions in the rings affects the absorption characteristics of the dyes. Poly(azomethine) macrocyclic dye **1** has absorption maxima in the invisible range at 297 (3.59), 316 (3.56), 329 (3.48) and 340 (3.60) nm.

The UV-Vis spectra show that bathochromic and hyperchromic effects can be obtained by introducing (nitrophenyl)azo group as in dye **3a**. This showed a considerable shift of 30 nm relative to **1**. Thus, electron displacement can be enhanced by electron-donating substituents on the coupled ring. The resulting increase in polarisability should result in a bathochromic effect (Fig. 1). A bathochromic shift can be obtained by replacement of the (3-nitrophenyl)azo with the (2,4-dinitrophenyl)azo group. In the last case absorption maxima are shifted in the long-wave direction, to 458 nm.

Furthermore, a bathochromic shift can be caused by introducing four 3-nitro- or (2,4-dinitrophenyl)azo substituents as in the dyes **4a** and **4b**. It is noticeable that displacement of the (3-nitrophenyl)azo with the (2,4-dinitrophenyl)azo group in the last case does not influence the absorption position, while it affects absorption intensity (hyperchromic effect).

Finally, introduction of the above mentioned nitrophenylazo groups causes fluorescence quenching.

Infrared Spectra

The infrared spectra of **3a**, **3b**, **4a** and **4b** contain characteristic bands at 3455–3400 cm^{-1} , which indicate phenolic O–H stretching. The strong bands, observed at 1609–1600 cm^{-1} indicate stretching vibration of the C–C aromatic skeleton. The bands at 825–815 and 1355–1349 cm^{-1} correspond to aromatic C–H and CH=N stretching, respectively. The stretching at 1532–1525 cm^{-1} corresponds to azo group. The bands at 1583–1575 and 1393–1380 cm^{-1} are due to the nitro group(s).

Kinetic Study

Kinetics of the azo coupling reaction were followed under pseudo-first-order conditions (in at least twenty-fold excess of **1**) by monitoring the appearance of the absorption band due to the product at 470 nm). Excellent pseudo-first-order kinetic plots covering at least two half-lives were ob-

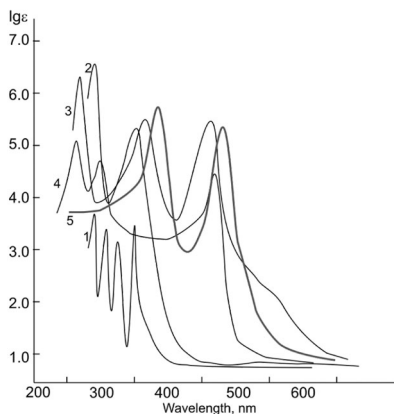


FIG. 1
UV-Vis spectra of dyes: 1 **1**, 2 **3a**, 3 **3b**, 4 **4a**, 5 **4b**

tained. Quantitative yields of azo coupling products were determined by comparison of the absorption at 470 nm in samples with those calculated using the molar absorption coefficient of an authentic sample of **3a**, **4a** and **4b**. The pseudo-first-order rate constants are 1.157×10^{-5} and $8.680 \times 10^{-6} \text{ s}^{-1}$ in water and chloroform, respectively.

Dyeing Performance

The disperse azo-poly(azomethine) dyes **3a**, **3b**, **4a** and **4b** were applied for polyester and Nylon fibers. The results are listed in Table I.

Monoazo-poly(azomethine) dyes **3a** and **3b** gave light brown and reddish-brown hues with good uniformity, brightness and depth of dyeing on the used fibers. Tetrasubstituted dyes **4a** and **4b** gave brown and dark brown hues, respectively, with excellent properties, as mentioned above. The dyed Nylon and polyester showed good fastness to light, washing, rubbing and perspiration and excellent fastness to sublimation. Insignificant changes of uniformity of dyeing after washing indicate good dye penetration and affinity to the employed fibers.

CONCLUSION

Twenty-membered macrocyclic poly(azomethine) dye **1** is a suitable azo coupling component capable of forming monoazo as well as tetrakisazo disperse dyes characterized by deep brown colors. It has been established that the final dye structure depends on the molar ratio of coupling agents. A molar ratio of 1:2 (**1/2a** or **2b**) gives monosubstituted macrocyclic poly(azomethine)s **3a** and **3b**, while the 1:20 molar ratio gives tetrasubstituted dyes **4a** and **4b**. The aqueous reaction medium is preferable due to a higher azo coupling rate constant ($1.157 \times 10^{-5} \text{ s}^{-1}$). The obtained disperse dyes are suitable for dyeing Nylon and polyester fibers with light reddish-brown to dark brown color with good uniformity of dyeing as well as light, washing and sublimation fastness.

EXPERIMENTAL

All of the chemicals of commercial grade were further purified by recrystallization or redistillation before use. The solvents were of spectroscopic grade. The IR spectra were obtained on a Thermo Nicolet spectrometer scanning between 4000–400 cm^{-1} using KBr plates. UV-Vis absorption spectra were measured in a CF-26 spectrometer (produced in Russia). Wavelengths are given in nm. Colors of crystals are given in CIELAB (L^* , a^* , b^*) coordinates. Elemental analysis was performed using a Heraeus CHNO-Rapid analyzer. ^1H NMR and

TABLE I
Color fastness and exhaustion of dyes **3a**, **3b**, **4a** and **4b** on fibers

Dye	Hue	Fiber	Exhaustion %	Fastness						
				light	wash	rubbing (dry)	rubbing (wet)	acid	alkaline	sublimation
3a	light-brown	polyester	75	4-5	4-5	4-5	4-5	4-5	3-4	5
3b	reddish-brown	polyester	78	4-5	4-5	4-5	4-5	4-5	4	5
4a	brown	polyester	80	4-5	4-5	4-5	4-5	4-5	4	5
4b	dark-brown	polyester	80	4-5	4-5	4-5	4-5	4-5	4	5
3a	reddish-brown	Nylon	80	4-5	4-5	4-5	4-5	4-5	3-4	5
3b	reddish-brown	Nylon	82	4-5	4-5	4-5	4-5	4-5	3-4	5
4a	brown	Nylon	85	4-5	4-5	4-5	4-5	4-5	4	5
4b	dark-brown	Nylon	85	4-5	4-5	4-5	4-5	4-5	4	5

^{13}C NMR spectra were recorded on a Varian Mercury-300VX instrument at 30 °C in DMSO. Chemical shifts are reported in ppm (δ -scale) relative to internal standard TMS (0.00 ppm). The operation frequency was 300 MHz for ^1H and 75.5 MHz for ^{13}C NMR. Coupling constants (J) are given in Hz. GC-MS spectra (70 eV, 150 μA , EI) were recorded on a Voyager GC/MS Finnigan instrument. Melting points were determined by an Electrothermal 9100. 3-Nitrobenzene-1-diazonium tetrafluoroborate (**2a**) and 2,4-dinitrobenzene-1-diazonium tetrafluoroborate (**2b**) were prepared from corresponding aromatic amines, sodium nitrite and tetrafluoroboric acid as described previously⁹. The rates of azo coupling of **1** and **2a** or **2b** (in at least twenty-fold excess) were determined by measuring the rate of appearance of absorption at 470 nm due to the dye. Plots of $\log(A_\infty - A_t)$ versus time were linear over at least two half-lives.

Fastness to light, sublimation, perspiration and washing fastness were assessed in accordance with valid state standards¹⁰⁻¹². The dyeing of polyester and Nylon fibers was carried out and exhaustion of the dyes was determined according to the literature¹³.

Azo Coupling in Aqueous Media (Method A)

A solution of 3-nitrobenzene-1-diazonium tetrafluoroborate (**2a**) or 2,4-dinitrobenzene-1-diazonium tetrafluoroborate (**2b**) (0.5–5 mmol) in water (25 ml) was added dropwise to a solution of poly(azomethine) **1** (0.119 g, 0.25 mmol) in aqueous sodium hydroxide (10%, 25 ml) over a period of 15 min with constant vigorous stirring. The reaction mixture was further stirred for a period of 24 h at ambient temperature and neutralized with hydrochloric acid (10%). The solids were filtered off, washed with water, dried and crystallized from ethanol. The obtained crystals were dissolved in a minimal quantity of methanol and adsorbed on silica gel, which was then placed on the top of a silica gel column. The column was eluted with toluene–ethyl acetate (3:1 v/v) and the product was isolated by evaporation of the solvent.

Azo Coupling in Non-Polar Media (Method B)

3-Nitrobenzene-1-diazonium tetrafluoroborate (**2a**) or 2,4-dinitrobenzene-1-diazonium tetrafluoroborate (**2b**) (0.5–5 mmol) was dissolved in chloroform (25 ml) by adding dibenzo-18-crown-6 in equimolar quantity as a phase transfer catalyst. After dissolution of **2a** or **2b** the solution was filtered and the filtrate was added to a solution of **1** (0.119 g, 0.25 mmol) in chloroform (15 ml). The reaction mixture was stirred at room temperature for 32 h. The precipitated crystals were isolated by filtration and the residue was washed with warm water, chloroform and cold methanol. Finally, the solid was crystallized from ethanol and purified by column chromatography as described in Method A.

Compound 3a. From **2a** (0.118 g, 0.5 mmol) and **1** (0.119 g, 0.25 mmol) by Method A: 0.091 g (0.145 mmol, 58%) of **3a** was obtained as brown crystals (ethanol, $L = 36$, $a = 29$, $b = 37$); m.p. 157–160 °C (ethanol); R_f 0.155 (toluene–ethyl acetate, 3:1). UV-Vis (ethanol), λ_{max} (log ϵ): 290 (6.43), 370 (5.18). IR: 3440 (OH), 2923 (CH), 1609 ($\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}$), 1570 (NO_2), 1527 (N=N), 1390 (NO_2), 1349 (C=N), 1257 (OH), 1172 ($\text{C}_{\text{Ar}}-\text{H}$), 817 ($\text{C}_{\text{Ar}}-\text{H}$). ^1H NMR: 8.52 s, 1 H (Ar-H); 8.31 d, 1 H, $J = 8.2$ (Ar-H); 8.05 d, 1 H, $J = 8.1$ (Ar-H); 8.00 s, 1 H (OH); 7.96 s, 3 H (OH); 7.78 t, 1 H, $J = 8.2$, 8.1 (Ar-H); 7.52 s, 1 H (Ar-H); 7.40 s, 1 H (Ar-H); 7.38 s, 3 H (Ar-H); 7.33 s, 3 H (Ar-H); 6.91 s, 4 H (NC-H); 6.85 d, 3 H, $J = 8.2$ (Ar-H). ^{13}C NMR: 163.7, 160.0, 155.2, 153.6, 148.2, 133.6, 131.6, 131.4, 130.0, 129.4, 129.2, 129.1, 126.1, 126.0, 125.7, 119.3, 119.1, 119.0, 116.5. GC-MS, m/z (%): 626 (100) [M^{+}], 579 (60),

503 (45), 489 (36), 475 (19), 238 (10), 150 (20), 136 (35), 122 (45), 46 (60). For $C_{34}H_{23}N_7O_6$ (625.6) calculated: 65.28% C, 3.71% H, 15.67% N; found: 65.55% C, 3.70% H, 15.60% N.

Compound 3b. From **2b** (0.141 g, 0.5 mmol) and **1** (0.119 g, 0.25 mmol) by Methods A and B. Method A: 0.1 g (0.15 mmol, 61%) and Method B: 0.107 g (0.16 mmol, 64%) of **3b** was obtained as yellowish-pink crystals (ethanol, $L = 87$, $a = 8$, $b = 34$); m.p. 205–208 °C (ethanol); R_f 0.145 (benzene–ethyl acetate, 3:1). UV-Vis (ethanol), λ_{max} (log ϵ): 262 (6.37), 356 (5.51), 458 (5.36). IR: 3450 (OH), 2930 (CH), 1605 ($C_{Ar}=C_{Ar}$), 1580 (NO_2), 1530 (N=N), 1393 (NO_2), 1355 (C=N), 1260 (OH), 1180 ($C_{Ar}-H$), 821 ($C_{Ar}-H$). 1H NMR: 8.55 s, 1 H (Ar-H); 8.39 d, 1 H, $J = 8.1$ (Ar-H); 8.32 d, 1 H, $J = 8.1$ (Ar-H); 8.01 s, 1 H (OH); 7.97 s, 3 H (OH); 7.53 s, 1 H (Ar-H); 7.42 s, 1 H (Ar-H); 7.39 s, 3 H (Ar-H); 7.34 s, 3 H (Ar-H); 6.95 s, 4 H (NC-H); 6.87 d, 3 H, $J = 8.2$ (Ar-H). ^{13}C NMR: 163.8, 160.1, 155.3, 153.7, 151.0, 144.9, 133.7, 131.7, 131.5, 130.4, 129.5, 129.2, 126.1, 125.8, 124.9, 120.4, 119.4, 119.1, 116.6. GC-MS, m/z (%): 670 (100) [M^{+}], 503 (63), 489 (36), 475 (49), 238 (48), 251 (46), 195 (49), 167 (63), 181 (36), 46 (80). For $C_{34}H_{22}N_8O_8$ (670.6) calculated: 60.90% C, 3.31% H, 16.71% N; found: 60.92% C, 3.30% H, 16.70% N.

Compound 4a. From **2a** (1.18 g, 5 mmol) and **1** (0.119 g, 0.25 mmol) by Method A: 0.155 g (0.145 mmol, 58%) of **4a** was obtained as reddish-brown crystals (ethanol, $L = 36$, $a = 29$, $b = 37$); m.p. 160–162 °C (ethanol); R_f 0.17 (toluene–ethyl acetate, 3:1). UV-Vis (ethanol), λ_{max} (log ϵ): 260 (5.00), 380 (4.29), 470 (4.05). IR: 3445 (OH), 2925 (CH), 1600 ($C_{Ar}=C_{Ar}$), 1575 (NO_2), 1532 (N=N), 1390 (NO_2), 1350 (C=N), 1260 (OH), 1182 ($C_{Ar}-H$), 825 ($C_{Ar}-H$). 1H NMR: 8.51 s, 4 H (Ar-H); 8.30 d, 4 H, $J = 8.2$ (Ar-H); 8.04 d, 4 H, $J = 8.1$ (Ar-H); 8.01 s, 4 H (OH); 7.78 t, 4 H, $J = 8.2$, 8.1 (Ar-H); 7.51 s, 4 H (Ar-H); 7.39 s, 4 H (Ar-H); 6.90 s, 4 H (NC-H). ^{13}C NMR: 163.5, 153.4, 148.2, 133.4, 129.8, 129.2, 128.9, 126.0, 125.8, 125.5, 155.2, 119.1, 118.8. GC-MS, m/z (%): 1073 (100) [M^{+}], 1026 (20), 888 (16), 584 (19), 528 (24), 472 (23), 150 (75), 136 (69), 122 (64), 46 (80). For $C_{52}H_{32}N_{16}O_{12}$ (1072.9) calculated: 58.21% C, 3.01% H, 20.89% N; found: 58.20% C, 3.10% H, 20.85% N.

Compound 4b. From **2b** (1.41 g, 5 mmol) and **1** (0.119 g, 0.25 mmol) by Methods A and B. Method A: 0.191 g (0.152 mmol, 61%) and Method B: 0.210 g (0.167 mmol, 67%) of **4b** was obtained as dark brown crystals (ethanol, $L = 28$, $a = 5$, $b = 21$); m.p. 218–220 °C (ethanol); R_f 0.145 (benzene–ethyl acetate, 3:1). UV-Vis (ethanol), λ_{max} (log ϵ): 378 (5.66), 463 (5.37). IR: 3455 (OH), 2932 (CH), 1608 ($C_{Ar}=C_{Ar}$), 1583 (NO_2), 1530 (N=N), 1380 (NO_2), 1355 (C=N), 1250 (OH), 1170 ($C_{Ar}-H$), 815 ($C_{Ar}-H$). 1H NMR: 8.54 s, 4 H (Ar-H); 8.38 d, 4 H, $J = 8.1$ (Ar-H); 8.31 d, 4 H, $J = 8.1$ (Ar-H); 8.00 s, 4 H (OH); 7.51 s, 4 H (Ar-H); 7.42 s, 4 H (Ar-H); 6.93 s, 4 H (NC-H). ^{13}C NMR: 167.3, 155.2, 153.7, 151.0, 144.8, 133.6, 130.3, 129.4, 126.4, 125.7, 124.8, 120.3, 119.3. GC-MS, m/z (%): 1253 (100) [M^{+}], 1068 (32), 884 (23), 528 (34), 472 (31), 46 (85). For $C_{52}H_{28}N_{20}O_{20}$ (1252.9) calculated: 49.85% C, 2.25% H, 22.36% N; found: 49.80% C, 2.28% H, 22.35% N.

REFERENCES

1. a) Herzog P., Dreier R.: EP 667 376; *Chem. Abstr.* **1995**, 123, 316875; b) Dado G. P.: US 5852179 (1998); *Chem. Abstr.* **1999**, 130, 67788; c) Shi C., Salmon S., Xu H.: WO 2003/040459; *Chem. Abstr.* **2003**, 138, 386807; d) Daus R., Grimm R., Heller J., Mura J.: WO 2000/011256; *Chem. Abstr.* **2000**, 132, 182002.
2. a) Karci F., Demirçali A.: *Dyes Pigments* **2006**, 71, 97; b) Qiana H.-F., Song X.-Y.: *Dyes Pigments* **2007**, 74, 672; c) Hallas G., Towns A. D.: *Dyes Pigments* **1997**, 35, 219;

- d) Hallas G., Choi J.-H.: *Dyes Pigments* **1999**, *40*, 119; e) Abd-El-Aziz A. S., Afifi T. H.: *Dyes Pigments* **2006**, *70*, 8.
3. Petrova-Miladinova P., Konstantinova T. N.: *Dyes Pigments* **2005**, *67*, 63.
4. a) Shen Y., Wang X., Xua S., Lia H.: *Curr. Appl. Phys.* **2007**, *7*, 96; b) Kima S.-H., Yoona S.-H., Kimb S.-H., Hanb E.-M.: *Dyes Pigments* **2005**, *64*, 45.
5. a) More S. V., Dongarkhadekar D. V., Chavan R. P., Jadhav W. N., Bhusure S. R., Pavar R. P.: *J. Indian Chem. Soc.* **2002**, *79*, 768; b) Vashi K., Naik H. B.: *Eur. J. Chem.* **2004**, *1*, 272.
6. Elizbarashvili E., Matitaishvili T., Topuria Kh.: *J. Braz. Chem. Soc.* **2007**, *18*, 1254.
7. Matitaishvili T., Lagvilava I., Elizbarashvili E.: *Georgia Chem. J.* **2008**, *8*, 56.
8. Chirakadze G. G., Elizbarashvili E. N., Baidoshvili P. O.: *Russ. J. Org. Chem.* **2000**, *36*, 1642.
9. Swain C. G., Rogers R. I.: *J. Am. Chem. Soc.* **1975**, *97*, 799.
10. State Standard 9733.3-083. Testing Methods of Dye Fastness Against Light under Artificial Exposure (in Russian).
11. State Standard 9733.3-083. Testing Methods of Dye Fastness Against Physico-chemical Treatment (in Russian).
12. State Standard 25993-83. Disperse dyes. Methods of Treatment (in Russian).
13. Melnikov B. N., Vinogradova G. I.: *The Application of Dyes*, p. 160. Khimiya, Moscow 1986.