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Synthesis, Spectral Properties and Application of Some Reactive Anthraquinone Dyes

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ABSTRACT

Four water soluble dyes containing the receive chloroacetyl group were synthesized and their spectral absorption and fluorescence characteristics investigated. Polyamide materials dyed with them showed very good colour characteristics and resistance to physicochemical effects. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Spectral properties, Anthraquinone, Polyamide.

INTRODUCTION

Aminoanthraquinone colourants are used for dyeing synthetic and natural textile materials [1–3]. The introduction of reactive groups into their structure permits their bonding via a strong covalent bond to the dyed material. In this manner an increased stability to external physicochemical effects is achieved [3, 4].

In this paper, the synthesis of some water soluble antraquinone derivatives containing the 1-chloroacetylamino group is reported and some of their properties are investigated.

RESULTS AND DISCUSSION

Dyes synthesis

The preparation of the dyes is outlined in Scheme 1. 1-Amino-2-sulpho-4-bromo-9,10-antraquinone interacted with primary and secondary amines *AH*

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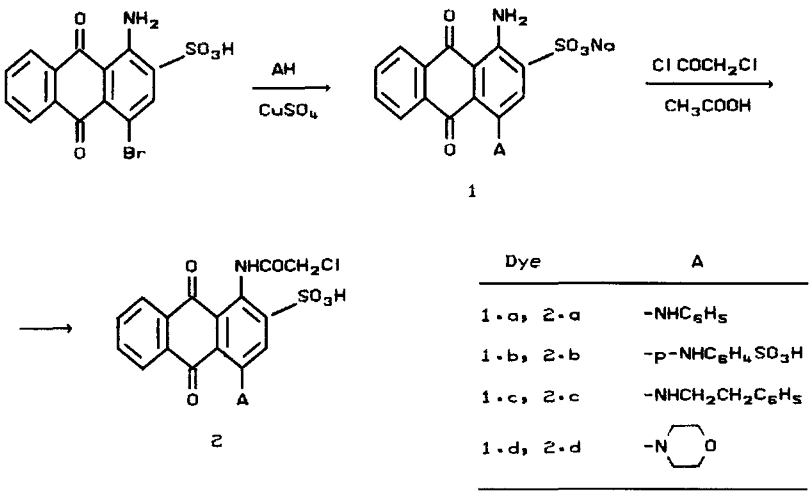

Dye	A
1·a, 2·a	$-NHC_6H_5$
1·b, 2·b	$-p-NHC_6H_4SO_3H$
1·c, 2·c	$-NHCH_2CH_2C_6H_5$
1·d, 2·d	-N O

Scheme 1.

in aqueous medium in the presence of copper sulphate for 6 h at 90°C to give product **1**. The product was isolated from the reaction medium by cooling the solution to 20°C and salting out with NaCl. Acylation of the primary amino group in **1** with acetylchloride was carried out (at 50°C during 2 h) to give **2**, which was isolated by pouring the reaction mixture into ethyl acetate and filtering the precipitate obtained.

Four water soluble anthraquinone dyes of the general formula **2**, containing the reactive chloroacetyl group were prepared in this manner. Relevant characterisation data are shown in Tables 1–3

Spectral investigations

The absorption spectra of dyes **1**, **2** in water, ethanol and dimethylformamide (DMF) were recorded, and the results obtained are shown in Tables 2 and 3. After the acylation of the primary amine group of dye **1**, a hypsochromic shift was observed in the absorption spectra of the dye **2** in all three solutions. This effect results from acylamino group acylation acquiring electron accepting properties, thus decreasing the donor–acceptor interaction with the carbonyl groups of the anthraquinone chromophone. The extent of the hypsochromic shift depends on the electron donating properties of substituents in the 4-position of the anthraquinone moiety, and on the solvent polarity. The results obtained have a qualitative, rather then quantitative, character. In aqueous solution, the dyes showed no fluorescence, in contrast

TABLE 1
Yield and Elemental Analysis Data of Dyes **1a–1d** and **2a–2d**

Dye	*Yield %*	*Formula (molecular mass)*	*Analysis (%) Calcd./Found*		
			C	*H*	*N*
1.a	78	$C_{20}H_{13}N_2O_5SNa$	57.68	3.12	6.73
		(416.1)	57.58	3.08	6.60
2.a	85	$C_{22}H_{15}N_2O_6SCl$	56.10	3.19	5.95
		(470.6)	55.90	3.14	5.85
1.b	75	$C_{20}H_{13}N_2O_8S_2Na$	48.37	2.62	5.64
		(496.2)	48.31	2.46	5.61
2.b	80	$C_{22}H_{15}N_2O_9S_2Cl$	47.94	2.72	5.08
		(550.7)	47.80	2.70	5.00
1.c	78	$C_{22}H_{17}N_2O_5SNa$	59.45	3.83	6.30
		(444.1)	59.38	3.78	6.25
2.c	89	$C_{24}H_{15}N_2O_6SCl$	57.76	3.81	5.62
		(498.5)	57.60	3.79	5.59
1.d	74	$C_{18}H_{15}N_2O_6SNa$	52.67	3.66	6.83
		(419.1)	52.50	3.60	6.79
2.d	78	$C_{20}H_{17}N_2O_7SCl$	51.66	3.66	6.03
		(464.6)	51.59	3.60	6.00

TABLE 2
Photochemical Properties of Dyes **1** and **2** in Water and Ethanol

Dye	*Water solution*			*Ethanol solution*					
	λ_{abs} (nm)	lgε	f	λ_{abs} (nm)	lgε	f	λ_{fl} (nm)	$\bar{\nu}_A - \bar{\nu}_F$ (cm^{-1})	τ ($10^8 s$)
1a	604	3.99	0.28	602	4.01	0.40	630	738	4.2
2a	552	3.98	0.24	528	3.97	0.36	606	2437	6.3
ab	590	4.03	0.25	592	3.98	0.35	608	444	5.8
2b	520	3.97	0.19	586	3.92	0.30	605	535	6.9
1c	592	3.99	0.23	628	3.96	0.34	640	349	4.8
2c	486	3.91	0.17	476	3.89	0.28	530	2140	5.7
1d	538	3.97	0.27	566	3.95	0.37	600	1002	3.1
2d	514	3.90	0.19	532	3.86	0.30	555	772	4.6

to measurements in ethanol and DMF. For the dye (**1.a**) no fluorescence in DMF was registered, while a very weak fluorescent emission was observed in ethanol solution. Stoke's shift were calculated using the relation:

$$\bar{\nu}_A - \bar{\nu}_F = \left(\frac{1}{\lambda_{abs}} - \frac{1}{\lambda_{fl}} \right) \times 10^7 \; cm^{-1}$$

where λ_{abs} and λ_{fl} are the values of the absorption and fluorescence maxima in nm.

TABLE 3
Photochemical Properties of Dyes **1** and **2** in Dimethylformamide

Dye	*Dimethylformamide solution*					
	λ_{abs} *(nm)*	$lg\varepsilon$	f	λ_{fl} *(nm)*	$\bar{\nu}_A - \bar{\nu}_F$ *(cm^{-1})*	τ *($10^8 s$)*
1a	626	3.95	0.42	—	—	—
2a	518	3.90	0.38	568	1699	3.9
1b	578	3.91	0.36	605	772	4.8
2b	537	3.87	0.27	611	2255	6.1
1c	610	3.90	0.31	632	570	5.5
2c	492	3.84	0.30	526	1314	6.1
1d	577	3.90	0.42	607	856	7.3
2d	538	3.83	0.37	608	2140	8.4

The largest Stoke's shift with ethanol as solvent, was observed for dye **2.a**, and the weakest for dye **1.c**, while in DMF a high shift was observed with dyes **2.a**, **2.b**, **2.d**. It seems that in DMF solution the Stoke's shift is considerable after acylation of the amino group, while in an ethanol solution this effect is valid only in the cases **1.a–2.a** and **1.c–2.c**.

The strength of the oscillator (f) is an important characteristic of the dye; f-values are calculated according to the relationship:

$$f = 4.32 \times 10^9 \Delta\nu_{1/2}\varepsilon_{max}$$

where $\Delta\nu_{1/2}$ is the width of the absorption band in cm^{-1} at $\varepsilon_{max}/2$.

In solutions of ethanol and DMF, the f-values were 0.27–0.40 and 0.27–0.42, respectively. In all three solvents, a decrease of the values of the oscillator strength was observed after the acylation of the amino group. This could be tentatively accounted for in terms of the hypsochromic effect after acylation.

The lifetime of the dyes in the exited state was calculated by the expression [5]:

$$\tau = \frac{3.33 \times 10^{-8}}{\nu_{max}^2 \int_{\nu_1}^{\nu_2} \varepsilon d\nu}$$

The results obtained are in the range $3–8 \times 10^{-8}$s and are presented in Tables 2 and 3.

The IR spectra of dyes **1** show an intense absorption band in the area 3350–3450 cm^{-1}, characteristic for the primary amino group; this band is absent in the spectra of dyes **2**. All the studied compounds contain a carbonyl group, that shows an intense absorption band in the area 1564–1591 cm^{-1}. An additional band appears for dyes **2**, which is characteristic for the vibrational oscillations of the $C = 0$ group of the acetyl fragment, and which appears at 1625–1668 cm^{-1}. A further intense band was observed in the spectra of all compounds at 1039–1046 cm^{-1}, characteristic of the vibrational oscillations of the $S = 0$ group.

Dyeing of polyamide materials with dyes 2

Dyeing of polyamide materials was carried out by the continuous method [6] at pH 5 in the presence of 5% Na_2SO_4 (owt) and 1% of dye **2**. The material was treated at 80°C for 30 min, after which it was extensively washed with water and then dried. Evaluation of the colours of the dyed materials was carried out by determining the x,y,Y and CIELab coordinates; the results obtained are presented in Table 4. It can be seen that the dyes show colours in the blue–red region, but of different shade and tint. Dyes **2** contain the reactive chloroacetyl group and during the dyeing process, this bond is broken and the dye interacts with the imine nitrogen atom of the polyamide macromolecule, forming a covalent bond. Besides this covalent bonding, an additional fixation of the dye on the polyamide material occurs by ionic bonds between the sulpho group of the dye and the protonated amino group of the polyamide. In this way the dye is fixed strongly to the textile material both by covalent and ionic groups, ensuring a stable colour effect towards wet treatments and solvents. The fact that the colour of the materials does not change after boiling for 1 h in a 1:1 water–ethanol solution, evidences as the covalent bond between the dye and the polyamide. It was established, by colorimetric measurement by the standard line method, that the extraction of the dyes from the dyebath was 95–98%, while the quality of chemically bound dye was 91–93% (Table 5). The values found (Table 5) reveal the high resistivity of the colouring effect towards physicochemical effects.

TABLE 4
Colour Data of Dyes **2a**–**2d** on Polyamide-6

Dye	*Cromaticity coordinates*			*CIELab-coordinates*		
	x	*y*	*Y*	*L**	*a**	*b**
2a	0.347	0.288	12.652	42.233	20.730	−5.654
2b	0.317	0.264	9.523	36.973	18.438	−12.640
2c	0.378	0.332	19.092	50.795	18.220	−7.516
2d	0.326	0.265	9.201	36.380	20.486	−20.486

TABLE 5
Fastness Properties of Dyes on Polyamide-6[a]

Dye	*Fastness*				*Extraction dye (%)*	*Chemically bound dye (%)*
	Light-fastness	*Alka-line*	*Washing*	*Sea water*		
2a	5–6	5	6–7	5	96	91
2b	5–6	5	6–7	5	95	91
2c	5–6	5	6–7	5	98	93
2d	5–6	5	6–7	5–6	95	91

[a] Dyeing at 1% dye

EXPERIMENTAL

Apparatus and techniques

UV/VIS spectra of the dyes were recorded in a solution of water, ethanol and dimethylformamide at a concentration of 1.10^{-4}M using a Hewlett–Packard UV/VIS 8452A spectrophotometer. Fluorescent measurements were carried out on a Perkin–Elmer MPF44 spectrophotometer and IR spectra (KBr) on a Perkin–Elmer FTIR 1600 spectrophotometer.

Colour space coordinate determinations (x,y,Y, and CIELab) of the materials were carried out using a Texflach ACS/DATACOLOR spectrophotometer.

General method for synthesis of dyes

First, 0.01 M bromoaminic acid was dissolved in 100 ml of water and 0.2 g copper sulphate and 0.01 M amine (AH) were added. The mixture was stirred for 6 h at 90°C, after which it was cooled to 20°C and the dye isolated by salting with NaCl, and drying.

Then 0.01 M of the prepared dye was dissolved in 50 ml glacial acetic acid and 0.02 M chloroacetylchloride was added dropwise at 50°C. The mixture was stirred for 2 h and, after cooling to room temperature, ethyl acetate was added until the acylated dye precipitated. The precipitate was filtered, washed with ice-water, and dried under vacuum at 40°C.

Dyeing of polyamide-6

The dyeing of polyamide-6 was carried out by the continuous method in the presence of 5%(owt) Na_2SO_4 at pH 5 (CH_3COOOH) [6].

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