

INVESTIGATION OF TWO TEXTILE ANTHRAQUINONE DYES PURITY

Andreia SANISLAV¹, Florina DUMITRU², Michaela Dina STĂNESCU³

The purity of two blue commercial dyes, often used in textile industry, have been analyzed. The purpose of the study is to reduce the pollution generated by the dyeing process by avoiding the presence in dyes of polluting compounds. The studied dyes are substituted 1,4- diamino-anthraquinone and belong to two different tinctorial groups, namely reactive dyes and acid dyes. The nomenclature established by Colour Index is: Acid Blue 62 and Reactive Blue 19, respectively. Based on the analysis of NMR and MS spectra, it has been established that while the acid dye is almost pure the reactive dye contains also secondary products from its degradation (alcohol and alkene). The corresponding alcohol is untaken by the textile material being a potential pollutant.

Keywords: Reactive Blue 19, AcidBlue 62, NMR and MS spectra

1. Introduction

The dyeing process is an important step for the finishing of textile materials. Based on the chromophore type classification, the azo dyes are most frequently applied on textile materials. This fact is due to their simple synthesis and to the possibility of obtaining a large spectrum of colors, with small modifications of the raw materials used in the synthesis [1a]. The second group of compounds, largely applied despite the lower versatility in their synthesis, is that of the anthraquinone dyes [1b]. The well known structure for anthraquinone dyes is that of the amino derivatives, mostly with the amino group in 1,4 positions. Two of such anthraquinone dyes had been studied.

The dye bath exhaustion is very important, a better yield reducing the dye presence in the waste waters and consequently the corresponding environmental pollution due to colour presence [2]. The dye uptake depends also of the initial dye purity. It seems of interest to establish the composition of the two studied

¹ Ph.D. student, Dept. of Organic Chemistry “C.D. Nenitzescu”, University POLITEHNICA of Bucharest, Romania

² Ass. Prof., Ph.D., Dept. of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania

³ Prof., “Aurel Vlaicu” University, Elena Dragoi 2, 310330 Arad, Romania, corresponding author: e-mail: stanescu@uav.ro

commercial dyes by using procedures of instrumental analysis like: NMR, MS and TLC.

The analyzed dyes are (see Fig. 1) the C.I. Acid Blue 62 (**1**) (1-amino-4-cyclohexylamino-9,10-dihydro-9,10-dioxoanthracene-2-sulfonic acid sodium salt; CAS 4368-56-3) and C.I. Reactive Blue 19 (**2**) [2-(3-(4-amino-9,10-dihydro-3-sulfo-9,10-dioxoanthracen-4-yl)amino-benzenesulfonyl)ethyl disodium sulfate; CAS 2580-17-1]:

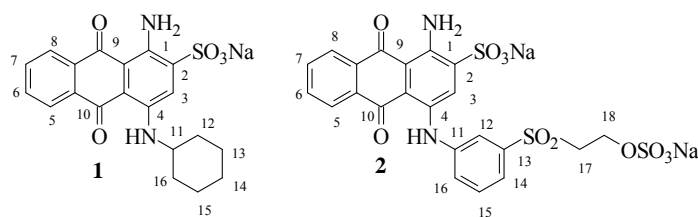


Fig. 1. The proposed structures for the two anthraquinone dyes **1** and **2**

A noninvasive investigation for establishing the composition of different industrial products seems to NMR spectroscopy. Such method is lately used for analyzing industrial products like wine and oil [3-6]. The NMR spectra of the commercial dyes coupled with MS and TLC may help to establish the purity of the compounds, and based on it to explain their dyeing behaviour, especially regarding the dye uptake on the textile material.

2. Experimental

Materials and methods

The two anthraquinone dyes, Acid Blue 62 (AB 62, **1**) and Reactive Blue 19 (RB 19, **2**) have been kindly supplied by Bezema AG–Switzerland.

The NMR spectra have been performed with a Bruker Avance DRX 400 spectrometer in deuterated dimethyl sulfoxide (DMSO-d₆) as solvent.

The MS spectra were carried out on a MSQ+ Thermo Fisher Scientific LC-MS spectrometer, using acetonitrile as carrier. The negative ion mode ionization was applied. The probe temperature is 500°C and cone voltage 40 V. Solutions of 10 mM in methanol were injected into the mass spectrometer at a flow rate of 0.5 mL min⁻¹, through a Surveyor LC Pump Plus. The analyses were performed in the range of 0-1500 m/z.

3. Results and Discussion

According to literature, the two studied compounds are usually produced from the same raw material, the bromaminic acid (**3**). The transformation of **3** into such dyes consists into a nucleophilic substitution of the bromine from **3**, by treatment

with the appropriate primary amine, using a catalytic reaction or in photochemical conditions [7-9]. The reaction for the preparation of 1,4-diaminoanthraquinones starting from **3** is illustrated in Fig. 2.

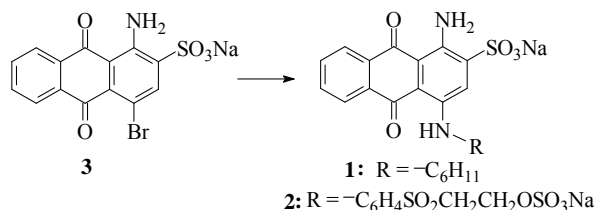


Fig. 2. A general method for preparing anthraquinone dyes

The AB 62 dye (**1**) is a bright blue solid, soluble in water, methanol and dimethyl sulphoxide (DMSO). The NMR spectrum was performed in DMSO d_6 , the solubility being optimum in this solvent. It presents the following ^1H -NMR spectrum (see Fig. 3):

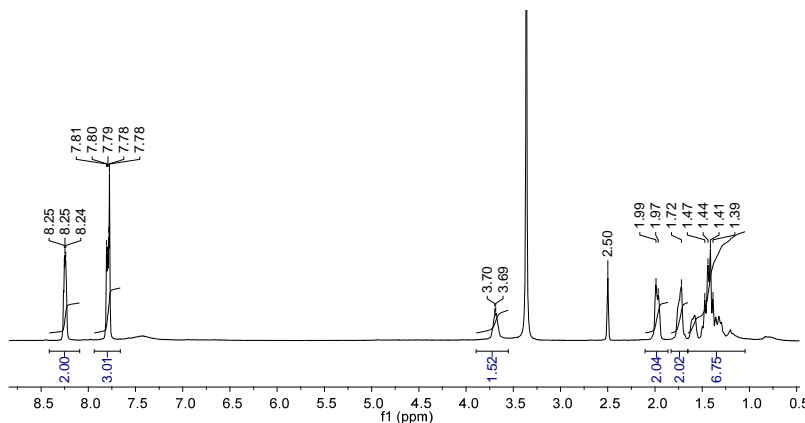


Fig. 3.1. ^1H -NMR spectrum of AB 62 dye in d_6 -DMSO

Both spectra (^1H - and ^{13}C -NMR) of dye AB 62 indicate only one component in the commercial product, corresponding to the proposed structure **1**.

As expected, the dye has five aromatic protons in the interval 8.30-7.70 ppm, four protons (H_5 - H_8) from the non substituted aromatic ring of anthraquinone and one (H_3) from the substituted ring. The chemical shift assignment was clarified by a series of 2D NMR experiments (COSY, HMQC, HMBC, or HSQC) which indicated the protons $\text{H}_{6,7}$ as the most deshielded ones [10].

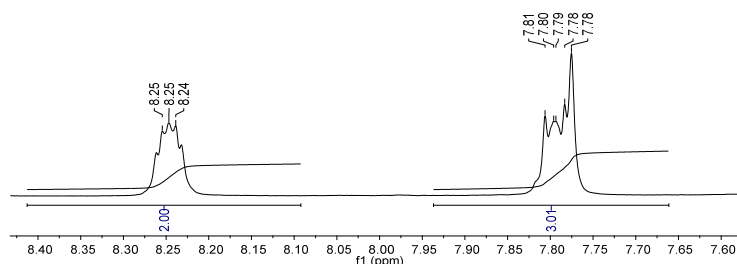


Fig.3.2. ^1H -NMR spectrum in DMSO-d_6 of the aromatic part of AB 62

In the aliphatic part there are the cyclohexane ring protons. Here, the most deshielded proton is the proton close to the NH group, namely H_{11} (2.60 ppm). The remaining protons of the aliphatic ring ($\text{H}_{12} - \text{H}_{16}$) resonate in the interval 1.30-2.10 ppm, showing a large multiplet. The proton of the NH group gives a peak at 3.70 ppm and those from NH_2 resonate most probably at 3.30 ppm. The solvent has two peaks, at 2.50 ppm (non deuterated methyl groups) and at 3.30 ppm (water) [11a]. No other proton signals are observed, confirming the high purity of the commercial product.

The same information is given by the ^{13}C -NMR spectrum (see Fig. 4):

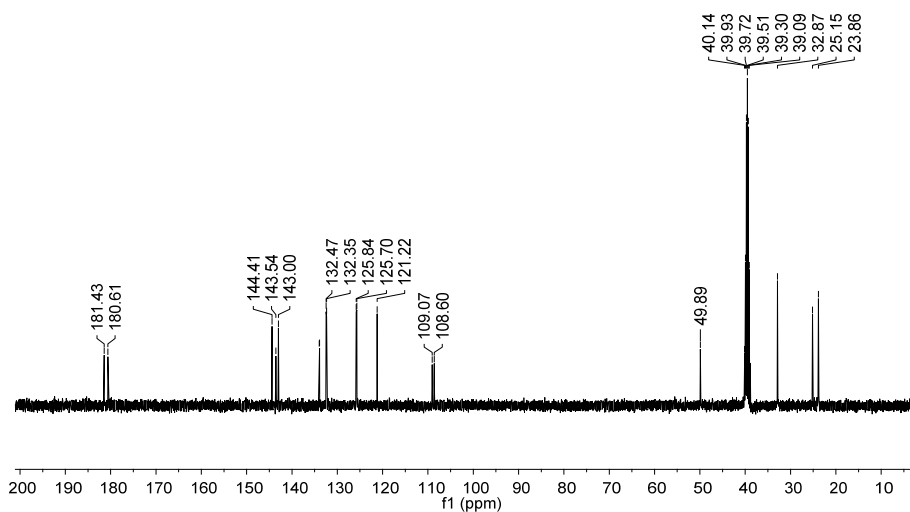


Fig. 4. ^{13}C -NMR spectrum of AB 62 dye in DMSO-d_6

The ^{13}C -NMR spectrum confirms the proposed structure with the two carbons from the CO groups (C_9 and C_{10}) at 180.51 and 181.43 ppm, followed by

all the twelve aromatic carbons, resonating in the interval 108.50-144.41 ppm. The saturated carbon connected to NH (C₁₁) presents a signal at 49.89 ppm, the other carbons from the cyclohexane moiety showing peaks at 23.86 (C₁₃,C₁₅); 25.15 (C₁₄); 33.84 (C₁₂,C₁₆) [10]. All the peaks are in accord with previously known data [11b].

The MS analysis also indicated only the presence of the ionized **1** (M-Na) with a peak with m/z of 399.22 (base peak) in anionic ionization.

For the reactive dye RB 19 (**2**) the results are different. The ¹H-NMR and MS spectra of the dye **2**, performed in the same conditions as for dye **1**, evidenced a mixture of compounds.

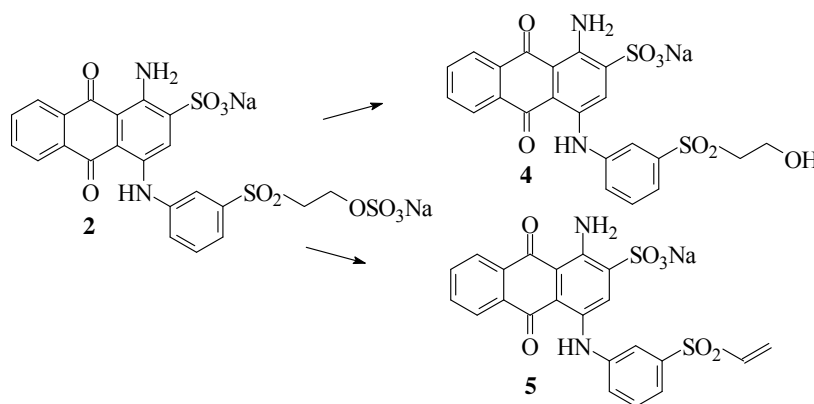


Fig.5. Transformations of RB 19 (**2**) by hydrolysis and elimination reactions

Beside **2** present with a peak (base peak) of the corresponding di-anion [$m/z = 289.81$; (M-2Na)/2] and traces of mono anion ($m/z = 603.52$; M-Na), also the degradation compounds, the alcohol **4** ($m/z = 501.69$; M-Na) and the alkene **5** ($m/z = 483.05$; M-Na) have been identified.

By analyzing the NMR spectrum of the commercial product the same conclusion is obvious. The commercial product contains beside the dye **2** its reaction products **4** and **5**. These compounds may be obtained by the sulfate group hydrolysis and/or by an elimination reaction of H₂SO₄, respectively (see Fig. 5).

Looking at the aliphatic part, peaks specific for the vinyl group of **5** may be observed. Traces of the compound **5** are designated by the peaks from 6.23-6.40 ppm (CH₂) and 7.11-7.18 ppm (CH) characteristic for the vinyl lateral chain (ABX [12]).

The saturated protons of the -CH₂-CH₂- lateral chain of both **2** and its corresponding alcohol **4** resonate at 3.67 (H_{17,17'}) and 3.98 (H_{18,18'}) giving two

triplets with the specific roofing effect. The protons H_{17, 17'} are more deshielded in comparison with H_{18, 18'}, due to the neighborhood of SO₂ group.

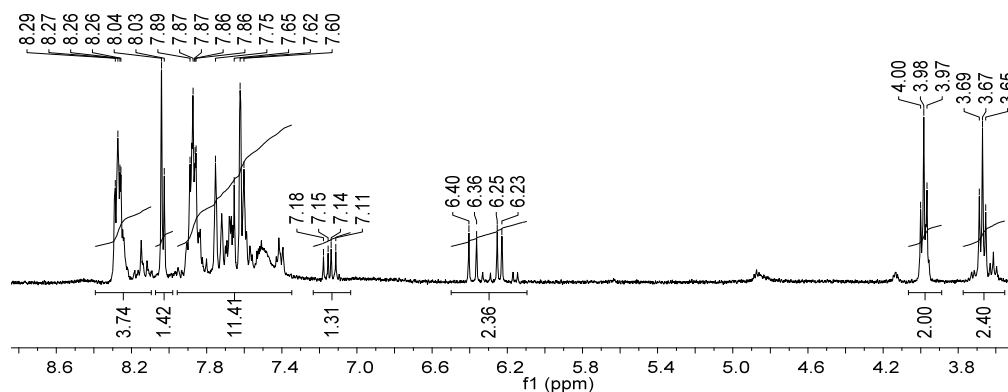


Fig.6. ¹H-NMR spectrum of commercial dye RB 19 (**2**) dye in DMSO-d₆

Comparatively, the spectrum of the hydrolysis product **4**, prepared by treatment of **2** with NaOH solution as described in literature [13], is presented in Fig. 7.1. One may see a less crowded aromatic part (7.30-8.35 ppm) with a possibility to recognize the protons of the anthraquinone moiety.

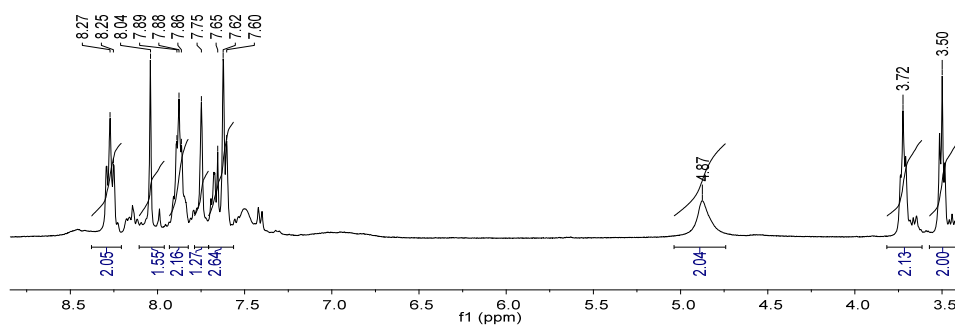


Fig.7.1. ¹H-NMR spectrum of the alcohol **4** in DMSO-d₆

It is worthwhile to mention that the position of H₃ peak is different for the two anthraquinone derivatives. While in compound **1** this proton appeared as a

singlet superposed on the H₈ and H₅ protons, in the compound **4** this proton is deshielded appearing as singlet between H_{6,7} and H_{5,8}.

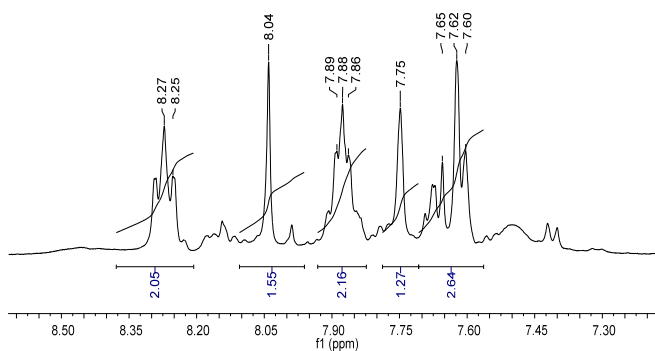


Fig.7.2. ¹H-NMR spectrum in DMSO-d₆ of the aromatic part of the alcohol **4**

Same information is given by the ¹³C-NMR spectrum.

By comparing the spectra of the compound **4** (Fig. 8) with that of the commercial dye (Fig. 9) one may see the differences, the commercial dye presenting a by far more complex spectrum due to the mixture of compounds therein.

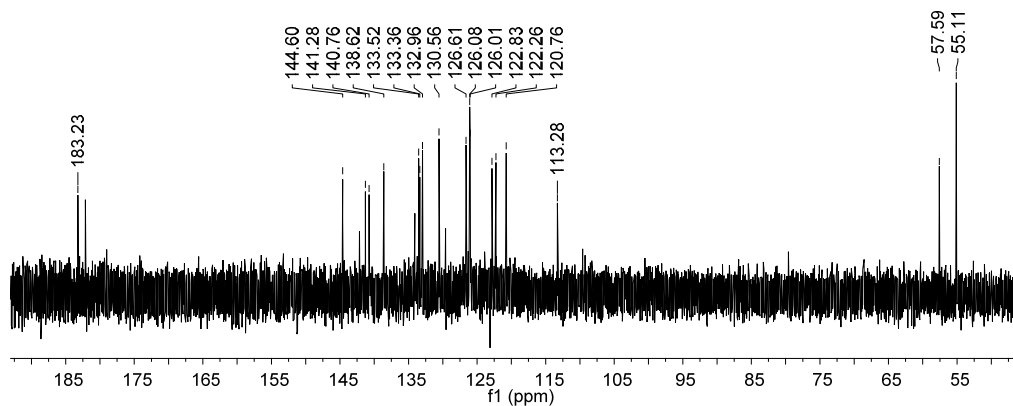


Fig.8. ¹³C-NMR spectrum of the alcohol **4** in DMSO-d₆

The spectrum clearly indicates the peaks for the two carbonyl groups (around 180 ppm) of the anthraquinone moiety, as well as the peaks for the two aliphatic carbons (C_{17} and C_{18}) between 50 and 60 ppm. The aromatic proton peaks, situated in the interval 144.61-113.28 ppm represent the carbon atoms (C_1 - C_8 , C_{4a} , C_{8a} , C_{9a} , C_{10a}) from the anthraquinone moiety and C_{11} - C_{16} , the carbon atoms from the benzene ring.

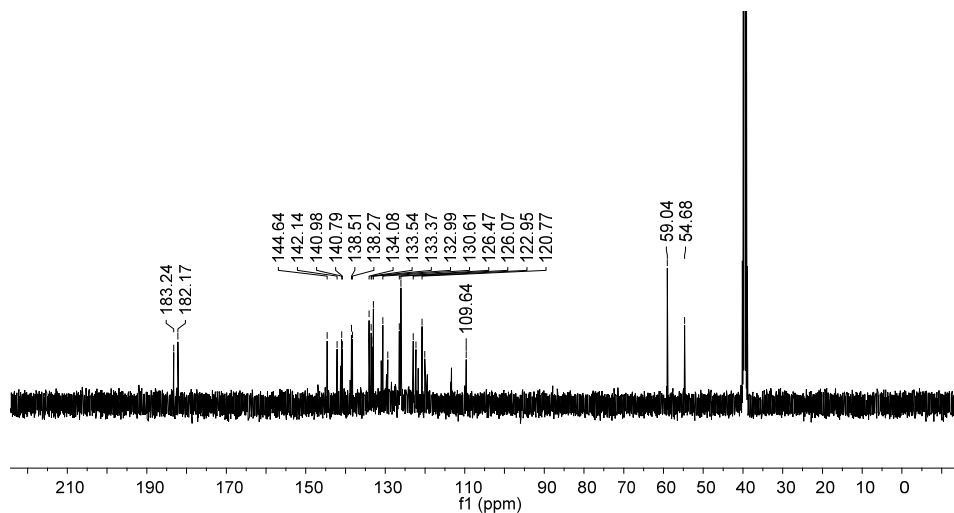


Fig.9. ^{13}C -NMR spectrum of the commercial dye RB 19 in d_6 -DMSO

The complex feature appearing for the aromatic carbon region, as well as the peaks around 110 ppm for the alkene protons present in the commercial dye RB 19 ^{13}C spectrum (Fig. 9) confirms the presence of the degradation products **4** and **5** beside the main component **2**.

A supplementary information is given by the TLC analysis on Merck alumina plates with solvent benzene/methanol in a volumetric ratio 1.5/1 when the presence of hydrolysis product **4** was evidenced in the commercial product **2** ($R_f = 0.53$).

4. Concluding remarks

Based on the experimental NMR and MS spectra of the two anthraquinone commercial dyes their composition may be proposed. It undoubtedly results that, while the acid dye AB 62 is practically pure, the reactive dye RB 19 contains from start its transformation products the corresponding alcohol **4** and the vinyl derivative **5**. While the compound **5** is in fact the intermediate in the dyeing process and can be valorized by addition to the textile fibers, the alcohol **4** does not react with the textile substrate and is eliminated in the dyeing waste water

raising its organic pollution due to its colour, which by reducing water transparency blocks the photosynthetic process [2]. Thus, a previous purification before dyeing is recommended for this dye, in order to eliminate the undesirable component 4.

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