

REACTIVE DYES BASED ON 2,4,6-TRICHLORO-PYRIMIDINE-5-CARBALDEHYDE ANCHOR GROUP

Adrian BARBATU¹, Izabela – Cristina STANCU², Raul - Augustin MITRAN³,
Ştefan TOMAS⁴

Acest articol prezintă sinteza și caracterizarea unor coloranți reactivi bazați pe gruparea ancoră 2,4,6-tricloro-5-formil pirimidină. În acești coloranți cromoforul este legat de gruparea ancoră prin intermediul grupării formil. Astfel, atomii de clor rămân disponibili pentru o fixare ulterioară pe fibrele textile.

This paper presents the synthesis and characterization of several reactive dyes based on 2,4,6-trichloropyrimidine-5-carbaldehyde anchor group, in which the cromophore is bonded to the anchor group by the formyl group. This way, the chlorine atoms remain available for further bonding to the textile fibers.

Keywords: 2,4,6-trichloropyrimidine-5-carbaldehyde, reactive dyes, anchor groups

1. Introduction

Reactive dyes are a category of dyes which attach to the substrate by chemical, covalent bonds formed between the anchor group contained in the dye and the functional groups present in the substrate. The first reactive dye was described in 1954 in [1] and marketed by ICI under the trade name Procion MX. The anchor group may contain one, or more identical, or different reactive groups [2], which allow the bonding to various substrates. Therefore, reactive dyes can be used to dye mixtures of fibers in an one-step process, which is more economically advantageous than the classical process, which involves separate dyeing of each fiber in the mixture.

Our main concern was to confirm the route for synthesizing the 2,4,6-trichloropyrimidine-5-carbaldehyde intermediate (**A**) previously described by Dehnert[3].

¹ PhD student, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania, e-mail: barbatu_adrian@yahoo.com

² Lecturer, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania

³ PhD. Eng., Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania

⁴ Reader, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania

Also, starting from the intermediate **A**, we synthesized four 2,4,6-trichloropyrimidine-5-carbaldehyde derivative azomethinic reactive dyes, in which the reactive group is represented by halogens placed in the 2- position.

Next, we also present the synthesis and characterization of several reactive dyes based on the 2,4,6-trichloro-pyrimidine-5-carbaldehyde anchor group with applicability in coloring textile fibers, paper and also biological substrates. In these dyes, the cromophore is attached to the anchor group through the formyl group.

2. Experimental

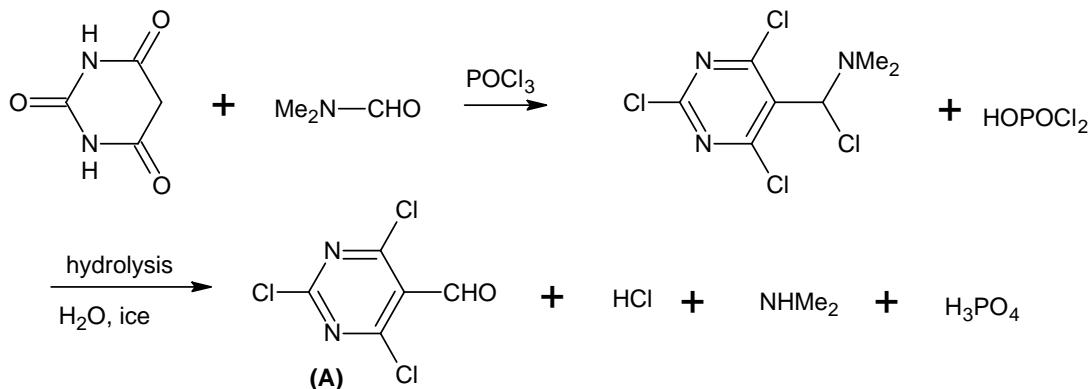
2.1 Materials

Dimethylformamide (DMF) (Merck) has been dried on molecular sieves prior to use.

Barbituric acid and POCl_3 (Sigma-Aldrich) have been used as such.

All aromatic amines (also Sigma-Aldrich) needed for dyes synthesis have been used without further purification.

Scheme 1 shows the first part of the synthetic procedure.



Scheme 1. General synthetic route to obtaining 2,4,6-trichloropyrimidine-5-carbaldehyde (**A**)

This reaction consists in the simultaneous carbonylic group synthesis and chlorine substitution of the -OH group in the barbituric acid.

2.2. Procedures

2.2.1 Synthesis of 2,4,6-trichloropyrimidine-5-carbaldehyde

The reaction is carried out starting from POCl_3 and DMF; the temperature dependency for various levels of temperature has been described (15°C , 50°C ,

85⁰C). Compared to the classical Vilsmeier synthesis [4], the above described reaction requires a higher molecular ratio of POCl₃ so that to generate chlorine atoms for the nucleophilic substitution.

Instead of a classical POCl₃: heterocycle ratio of 1:1, this reaction requires a ratio of 7:1 (or even up to 10:1). We have employed this method as it is considered to be the best approach to synthesizing 2,4,6-trichloropyrimidine-5-carbaldehyde.

The synthesis of the intermediate has been carried out in a 3-necked round bottomed flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. The experiment had to be performed inside the fume hood due to the rise of HCl vapors.

Subsequently, the flask has been cooled on an ice bath and 66 mL (710 mmol) POCl₃ has been slowly added, dropwise, over 9.32 mL (100 mmol) DMF, under continuous stirring. After ice cooling the mixture of POCl₃ – DMF, 12.8g (100 mmol) barbituric acid has been added in portions under vigorous stirring until the mixture practically solidifies. During this time a change in the color of the mixture, from orange-yellow to yellowish white has been noticed. The time required in forming the solid mixture varied largely with the temperature of the mixture of DMF – POCl₃; for instance, we have noticed that when the temperature range is higher than 0 – 10⁰C, the forming time was almost 4 hrs and the yields diminished drastically.

After the forming of the solid mixture, we have started cautiously increasing the temperature to 50⁰C. The mixture has been maintained at this temperature for 6 hrs. Either sudden changes in temperature or exceeding the 50⁰C mark may lead to a dramatic decrease in the yield (below 10%).

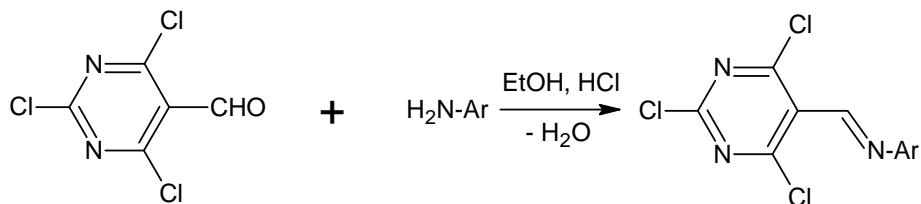
After maintaining the reaction mixture at 50⁰C for 6 hrs, the temperature has been again increased slowly up to 85⁰C. At this temperature a new change in the color of the mixture has been noticed, from yellowish white to red-yellow.

Next, the mixture has been maintained at a temperature of 85⁰C for 20 hrs. Again, it must be noted that a strict control over the reaction time and temperature is a key factor to obtaining high yields.

A yellowish white precipitate of 2,4,6-trichloro-pyrimidine-5-carbaldehyde has been obtained. The precipitate has been filtered using a Büchner funnel and then dried. The product has been purified with sodium metabisulphite. We have obtained 10g A with 46% yield.

The melting point of the obtained 2,4,6-trichloro-5-formyl-pyrimidine has been determined to be 130-131⁰C.

2.2.2. Synthesis of various reactive dyes



Scheme 2. Reaction of **A** with aromatic amines

Dye 1. 10 mL of absolute ethyl alcohol, 1g (4.7 mmol) 2,4,6-trichloro-5-formyl-pyrimidine, 0.25g (2.3 mmol) *o*-phenylenediamine and 2 mL HCl 32% (mass %) have been added to a round bottom flask equipped with an ascending condenser and a water bath. The temperature has been increased until the refluxing of the solvent began, maintaining this state for 4 hrs. After a 24 hrs cooling, the reaction mass has been subjected to filtering and then drying. Post drying, 0.7g (2.3 mmol) dark brown dye (**1**) (m.p. = 246-247°C) have been obtained.

This working procedure has been repeated for *p*-phenylenediamine, α -naphthylamine and *p*-amino nitro benzene, which yielded compounds **2**, **3**, and **4**. The results are presented in Table 1.

The compounds that we obtained were analyzed by means of FT-IR, UV and 3D fluorescence spectra [5]. The FT-IR spectra were taken on a Jasco 6200 spectrometer equipped with a Specac Golden Gate attenuated total reflectance (ATR) accessory, using a resolution of 4 cm⁻¹ and an accumulation of 60 spectra, in the 4000-400 cm⁻¹ wave number region.

The 3D fluorescence spectra have been acquired using a JASCO FP-6500 fluorescence spectrophotometer, at 1 nm intervals for emission and 5 nm intervals for excitation, a response time of 0.02 seconds, high sensitivity, and a scanning speed of 1000 nm/minute.

Unless otherwise stated, all the samples consisted in methanol solutions of 1 \times 10⁻⁴ M concentration.

Excitation and emission maxima have been computed using the “Emission search viewer” function provided by *JASCO Spectral Manager* software.

3. Results and discussion

Several reactive dyes have been obtained by the method described in Section 2.

Table 1

Various dyes obtained by condensation

Dye	Structure	m.p.(°C)	η(%)
1		246-247	61
2		237-238	70
3		190-191	57
4		220-221	51

FT-IR spectrum for compound A

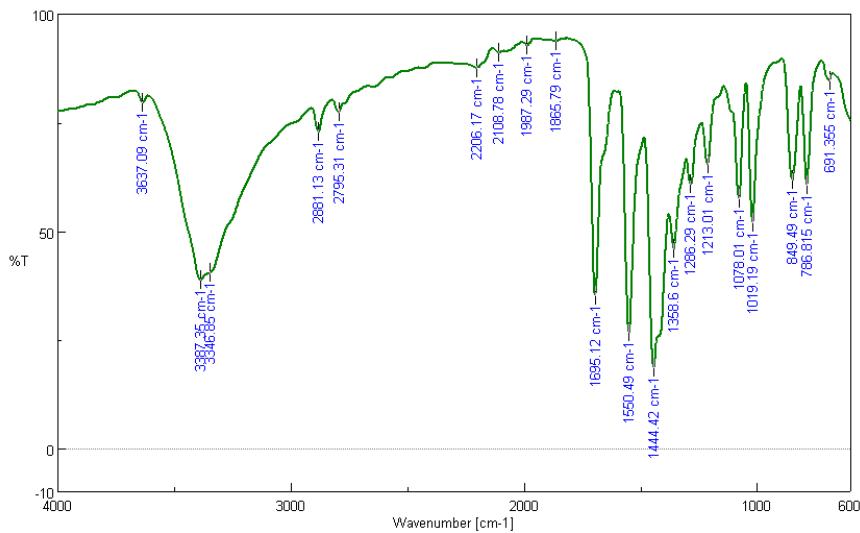


Fig. 1 FT-IR spectrum of A

The relevant peaks are at 1695 cm^{-1} (stretch), which can be attributed to -C=O formylic bond, 2881 cm^{-1} and 2795 cm^{-1} , which indicate the $=\text{C-H}$ bond from a formyl group. The peaks at 1550 cm^{-1} and 1444 cm^{-1} correspond to $-\text{C=N}$ bonds. The peak at 691 cm^{-1} can be attributed to C-Cl bond.

UV spectrum for compound A

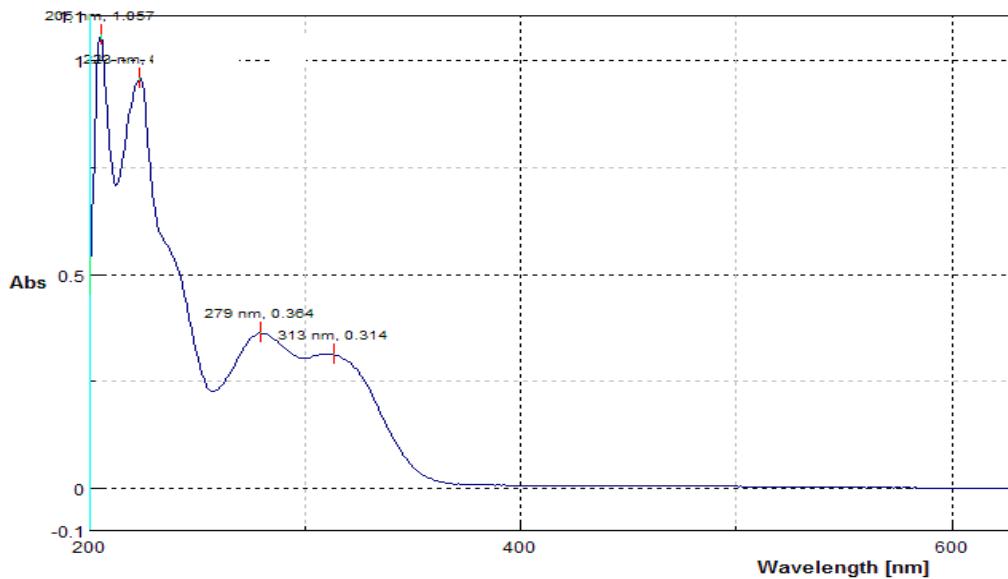


Fig. 2. UV spectrum for compound A

The 279 nm UV absorption peak can be attributed to the $\pi-\pi^*$ transition of the aromatic ring. Likewise, the 313 nm absorption peak is caused by the $n-\pi^*$ transition of the formyl substituent. This lower energy transition is another proof for the presence of the formyl group we planned to obtain.

The UV absorption peak of 210 nm can be attributed to C=N and C=C bonds.

Using Lambert-Beer law we determined ϵ (extinction coefficient) to be 2200. This value is high enough to allow usage of UV-VIS spectroscopy for quantitative measurement of **A** in solutions. Compound **A** has been found to possess fluorescent properties, having an emission maximum of 327 nm and excitation maximum of 280 nm.

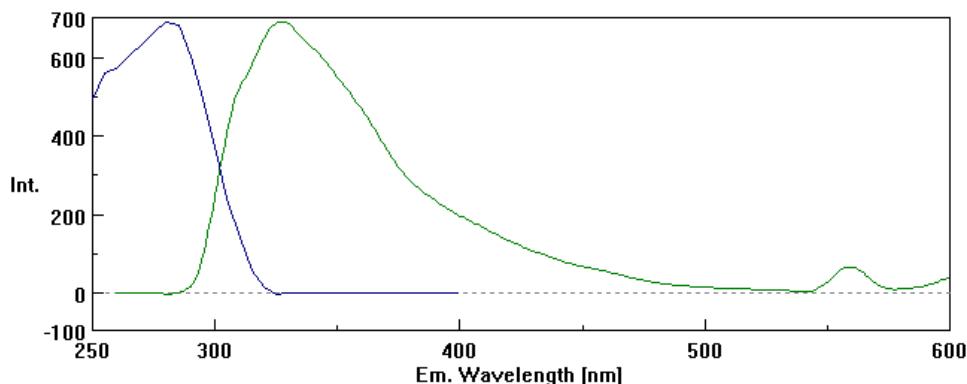


Fig. 3. Excitation and emission maxima for **A**

Fig. 3 shows the excitation and emission maxima as computed with the Emission Search Viewer. One may notice the typical mirror image characteristic for the fluorescent compounds.

4. Conclusions

Throughout our work we confirmed the route for synthesizing the 5-formyl-2,4,6-trichloropyrimidinic intermediate previously described by Dehnert.

Also, we synthesized four trichloro-pyrimidine type reactive dyes in which the cromophore is linked to the anchor group by an iminic bond. This way chlorine atoms remain available in the 2- position. These atoms can be nucleophilically substituted by OH groups in the fiber at relatively low temperatures.

Acknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/61178.

R E F E R E N C E S

- [1] *I.D. Rattee, W.E. Stephen*, Canadian Intellectual Property Office, CA589873, 1954
- [2] *K. Hunger*, Industrial Dyes: Chemistry, Properties, Applications, Wiley-VCH, Weinheim, 2003, pp 114-116.
- [3] *J. Dehnert*, Ger. Offen. DE 3603797, 1987 (Chem. Abstr. 1988, 108, 7511z)
- [4] *M.B. Smith, J. March*, March's Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 6th edition, J. Wiley and Sons, Inc, 2007, p 724
- [5] *R.A. Mitran, A.C. Boscornea, I.C. Stancu, S. Tomas*, "Some unusual spectral properties of 6-azauracil derivatives", inUPB Sci. Bull., Series B, **vol 73**, Iss. 1, 2011.