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New Azo Carboxylic Dyes Derived from Eugenol: Synthesis and Preliminary Application to Polyamide †

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Abstract: A series of azo dyes containing eugenol, the major phenolic compound in clove (*Syzygium aromaticum*) essential oil, was synthesized by coupling reactions of diazonium salts of different amines based on 3-aminobenzoic acid with eugenol. The new eugenol-based azo dyes were fully characterized by the usual analytical techniques and used in preliminary reactive dyeing tests on polyamide fabric to determine the colour fastness and staining under domestic washing conditions. The results obtained revealed the potential of these dyes for applications in the textile area.

Keywords: eugenol derivatives; essential oils; azo dyes

1. Introduction

Every day, dyeing is used on a large scale in order to optimize and improve the aesthetics of textiles to face the growth of the textile industry [1]. Consequently, this growth has negative impact on the environment as the textile industry is a significant contributor to environmental pollution [2]. To face this problem, dyes derived from natural compounds are a new and eco-friendly alternative to synthetic dyes [3].

Eugenol, a natural compound present in clove oil, enables the azo coupling reaction that leads to the formation of azo dyes [4–6]. As is well-known, azo dyes are the most important synthetic colourants that have been widely used in textile manufacturing [7].

From a chemical perspective, azo derivatives consist of aryl/alkyl and –N=N– groups, which are usually synthesized by the diazotization of primary aromatic amines and the coupling of the corresponding diazonium salts with an activated aromatic substrate [8,9]. Azo reactive dyes are characterized by having chemical groups capable of forming covalent bonds with textile substrates through a specific dye activation process [10].

Considering all of these facts, the synthesis and full characterization of three azo dyes from diazonium salts of 3-aminobenzoic acids and eugenol was conducted. Polyamide fabric was dyed with the dyes that were obtained and the colour fastness was evaluated under domestic washing conditions.

2. Results and Discussion

Synthesis of Eugenol Derivatives

Eugenol dyes **3a–c** were synthesized by coupling eugenol with different aromatic amines. The reaction from 3-aminobenzoic acid **1a**, 3-amino-2-methylbenzoic acid **1b** or 3-amino-4-methylbenzoic acid **1c** with sodium nitrite, under acidic conditions, resulted in the formation of the corresponding diazonium salts, which reacted with eugenol (4-allyl-2-methoxyphenol), in the presence of sodium hydroxide, to give 3-((5-allyl-2-hydroxy-3-methoxyphenyl)diazenyl)benzoic acid **3a**, 3-((5-allyl-2-hydroxy-3-methoxyphenyl)diazenyl)-2-methylbenzoic acid **3b** and 3-((5-allyl-2-hydroxy-3-methoxyphenyl)diazenyl)-4-methylbenzoic acid **3c**, respectively (Scheme 1).

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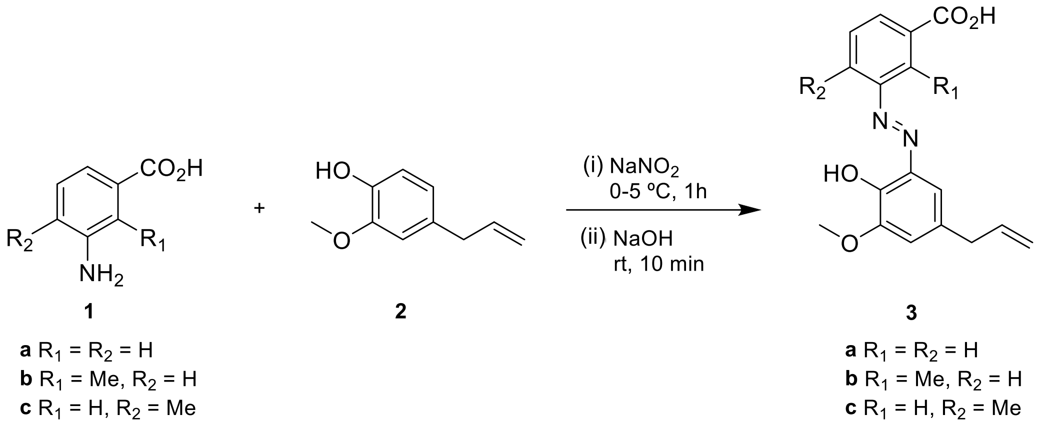

Scheme 1. Synthesis of eugenol carboxylic dyes **3a**–**c**.

Compounds **3a**–**c** were obtained as orange (**3a**) or red-brown solids (**3b**,**c**) in 40 to 76% yields, and were fully characterized by the usual analytical techniques.

Their ^{1}H NMR spectra showed the different characteristic signals for aliphatic protons, namely for the methyl (δ 2.69–2.80 ppm), methoxyl (δ 3.84–3.86 ppm) and methylenic groups (δ at about 3.4 ppm), as well as the expected protons for the eugenol's double bond as multiplets, CH_2 (δ 5.05–5.17 ppm) and CH (δ 5.95–6.05 ppm), in addition to the aromatic protons from eugenol H-4 and H-6 as doublets (δ 6.97–7.23 ppm), and the amines, H-2, H-4, H-5 and H-6 (δ 7.56–8.44 ppm).

The ^{13}C NMR spectra of all compounds showed the signals of the aliphatic carbons from the methyl (δ 14.25–17.48 ppm), methylene groups (δ at about 38.90 ppm) and methoxyl (δ at about 56.06 ppm), in addition to the carbons of the aromatic rings (δ 111.92–151.67 ppm) and the carbonyl groups (δ 166.79–168.82 ppm).

The FTIR spectra of respective dyes also confirmed the presence of CO_2H groups, showing the corresponding C=O stretching vibration bands at 1679 cm^{-1}. The –N=N– groups stand out at 1425 cm^{-1}, which indicates the asymmetric stretching of the respective bond.

The UV-visible absorption spectra of dyes **3a**–**c** in solvents of different polarities revealed wavelengths of maximum absorption (λ_{max}) in the range 341–347 nm (Figure 1), with a molar extinction coefficient (ε), shown as log ε, between 3.84 and 4.39 (Table 1). The presence of the methyl group influences the λ_{max}, since it causes a slight bathochromic shift in dyes **3b** and **3c** compared to **3a**. The λ_{max} is identical in **3b** and **3c** because they are constitutional isomers (only the position of the methyl group changes).

Table 1. The absorption data of compounds **3a**–**c** at 1.0 × 10^{-4} M in different solvents.

Solvent	**Dye**					
	3a		**3b**		**3c**	
	λ_{max}	**log ε**	**λ_{max}**	**log ε**	**λ_{max}**	**log ε**
EtOH	342	4.34	347	4.26	347	4.18
MeCN	341	4.23	347	4.27	347	4.25
AcOEt	342	4.25	347	4.28	348	4.19
DMF	344	4.16	350	4.22	350	4.18
H_2O	341	3.84	350	3.88	357	4.10
DCM	342	4.39	349	4.21	348	4.20
MeOH	341	4.34	347	4.23	346	4.17

The dyeing of polyamide fabrics was performed at 100 °C for 30 min by using ethyl chloroformate activation of the carboxylic acid group of dyes **3a**–**c** for the reactive dyeing of the textile material after which the coloured samples were submitted to the ISO 105 CO6, AS1 test [11,12]. The results of wash fastness shown in Table 2 demonstrate that eugenol dyes **3a–c** exhibited moderate or good fastness levels to washing, with a change in colour of 3 or 4 (**3b**) and colour staining of 5 (with exception of **3c** in cotton) in the grey scale.

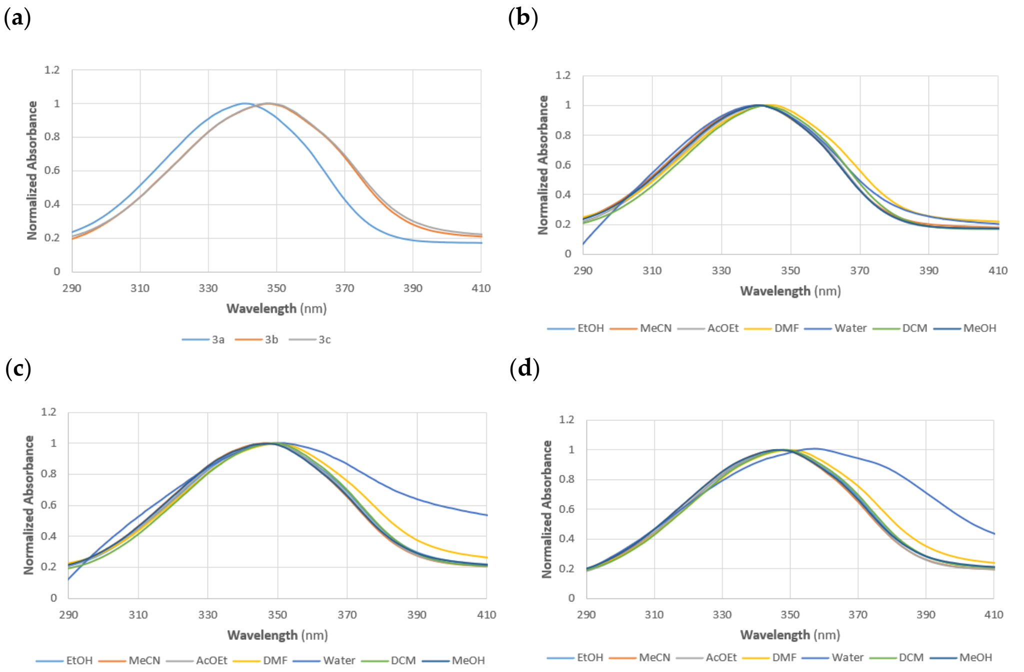

Figure 1. Absorption spectra of dyes **3a–c** in absolute ethanol (**a**). Absorption spectra of dyes **3a** (**b**), **3b** (**c**) and **3c** (**d**) in different solvents.

The FTIR spectra of the dyed fabric (Nylon 6) suggested that the previously activated dye bonded to polyamide through the disappearance of the band attributed to the stretching of the N-H bond at 3297 cm^{-1} and the appearance of a band associated with the C=O group of an imide at 1713 cm^{-1}, which was previously at 1631 cm^{-1}, due to the C=O group of an amide (Figures 2 and 3).

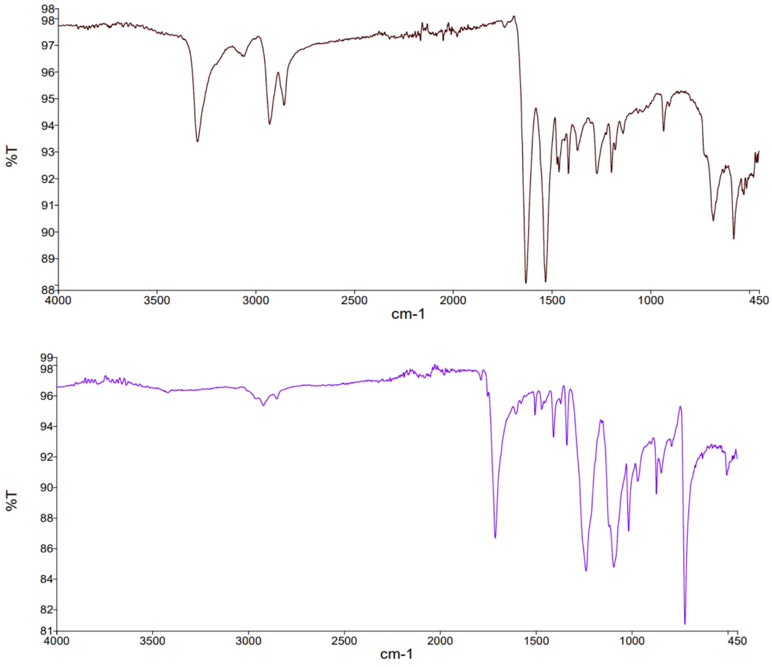

Figure 2. FTIR spectra of polyamide fabric (in brown) and the dyed polyamide with the dye **3b** (in purple).

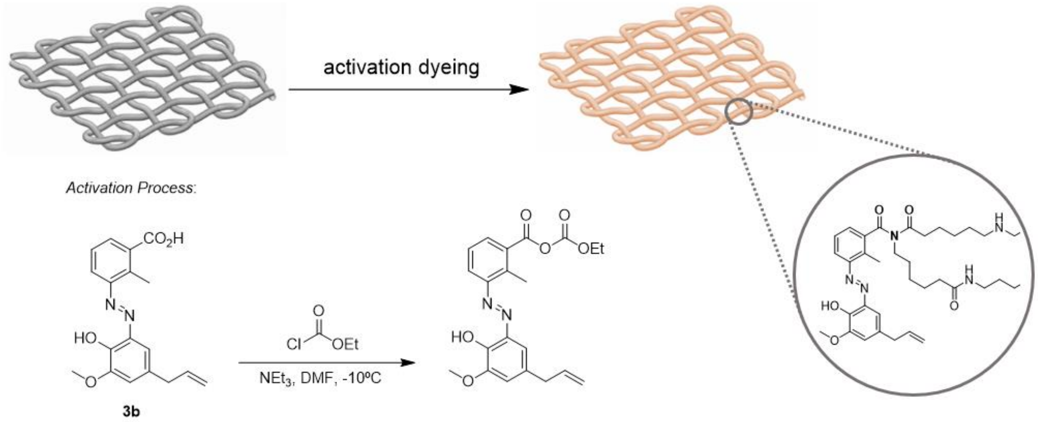

Figure 3. Dyeing approach by dye **3b** activation.

Table 2. Washing fastness indices of dyes with colours **3a**–**c**.

Dye	Change in Shade	Staining	
		Wool	Cotton
3a	3	5	5
3b	4	5	5
3c	3	5	4

3. Experimental Section

3.1. Typical Procedure for the Preparation of Compounds 3a–c (Illustrated for 3a)

A mixture of 3-aminobenzoic acid **1a** (0.500 g, 3.65×10^{-3} mol, 2 equiv), 1 M HCl (7.5 mL) and 6 M HCl (0.42 mL) was cooled to 0–5 °C. Aqueous sodium nitrite (0.251 g, 1.83×10^{-3} mol, 1 equiv, in 1 mL of water) was added and the reaction mixture was stirred for 45 min. The diazonium salt solution previously prepared was added dropwise to a solution of eugenol, 4-allyl-2-methoxyphenol **2** (0.300 g, 1.83×10^{-3} mol, 1 equiv) in NaOH (0.120 g, 3.00×10^{-3} mol, 1.6 equiv) and H_2O (1 mL). The precipitated dye was filtered, washed with cold water and diethyl ether, and dried. The crude product was subjected to flash column chromatography on silica gel, with DCM:MeOH, mixtures of increasing polarity, as eluent giving 3-((5-allyl-2-hydroxy-3-methoxyphenyl)diazenyl)benzoic acid **3a** as an orange solid (0.221 g, 40% yield). R_f = 0.63 (silica; dicholoromethane:methanol 90:10), m.p. = 127–129 °C. IR ($\upsilon_{max.}$): 2844, 2565, 1679, 1639, 1606, 1575, 1495, 1480, 1455, 1424, 1379, 1308, 1293, 1263, 1224, 1143, 1102, 1074, 905, 847, 762 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ_H 3.41 (2H, d, J = 6.8 Hz, CH_2Ph), 3.84 (3H, s, OCH_3), 5.05–5.14 (2H, m, CH=CH_2), 5.95–6.02 (1H, m, CH=CH$_2$), 6.98 (1H, d, J = 2.0 Hz, H-4), 7.17 (1H, d, J = 2.0 Hz, H-6), 7.70 (1H, t, J = 8.0 Hz, H-5 Ph-COOH), 8.07 (1H, dt, J = 8.0 and 1.6 Hz, H-4 Ph-COOH), 8.22 (1H, dq, J = 8.0 and 2.0 Hz, H-6 Ph-COOH), 8.44 (1H, t, J = 1.6 Hz, H-2 Ph-COOH), 10.60 (1H, s, OH), 13.25 (1H, br s, COOH) ppm. ^{13}C NMR (DMSO-d_6, 100 MHz): δ_C 38.93 (CH_2Ph), 56.06 (OCH_3), 111.92 (C-6), 115.90 (C-4), 116.00 (CH=CH_2), 122.79 (C-2 Ph-COOH), 127.06 (C-6 Ph-COOH), 129.75 (C5 Ph-COOH), 130.35 (C-1), 131.29 (C-4 Ph-COOH), 132.19 (C-1 Ph-COOH), 137.53 (CH=CH_2), 138.50 (C-5), 144.10 (C-2), 149.11 (C-3), 151.67 (C-3 Ph-COOH), 166.79 (COOH) ppm.

3.2. Typical Procedure for Dyeing of Polyamide Fabric (Illustrated for 3a)

To a cooled solution of the dye **3a** (0.015 g, 4.80×10^{-4} mol) in DMF (1.25 mL), triethylamine (0.020 mL, 1.44×10^{-3} mol) and ethyl chloroformate (0.014 mL, 1.44×10^{-3} mol) were added and the solution was stirred for 30 min. The triethylamine hydrochloride was filtered off and after adding water (100 mL) and the polyamide fabric (0.750 g) (the concentration of the dye in the dye bath was 2% of the fibre weight with liquor ratio 67:1) the mixture was stirred for 30 min at 100 °C. The fabric was removed, washed, and boiled for 15 min in water with Kieralon OLB soap (4 g/L) and, after drying, submitted to the ISO 105 C06-AS1 test [11,12].

4. Conclusions

Three azo carboxylic dyes that incorporate the eugenol unit in their structures displayed absorption maxima at 342–347 nm (in absolute ethanol), were obtained in good yields and applied though a reactive dyeing process, where they showed moderate to good fastness levels to washing on polyamide fabric. Encouraged by these results, new dyes will be synthesized and used in the dyeing of other textile materials in order to generate more knowledge in terms of the potential application of these types of semi-synthetic dyes based on eugenol in the textile industry.

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