



Microwave Assists the Synthesis of Pyridone azo Dyes and their Application in Polyester Printing

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Available online at: www.isca.in

Received 20th June 2012, revised 28th June 2012, accepted 11th July 2012

Abstract

In this study microwave assists synthesis of new class arylazopyridone dyes, where these dyes synthesized from corresponding dianilides, which coupled with some diazotized aromatic amines to give azodisperse dye which react with cyanoacetamide to form crossponding derivatives of pyridone azo dyes. The structure of these dyes were confirmed by IR, H-NMR, Mass spectra and element analysis. The fastness properties of silk screen printed polyester using these synthesized dyes have been investigated. The prints possess very good fastness properties of washing, rubbing, perspiration and light fastness.

Keywords: Microwave, pyridone azo dyes, textile printing.

Introduction

A microwave is a form of electromagnetic energy, which falls at the lower end of the electromagnetic spectrum and is defined in a measurement of frequency as 300 to 300,000 Megahertz, corresponding to wavelengths of 1 cm to 1 m. The microwave region of the electromagnetic spectrum lies between infrared and radio frequencies 2, 3. Wavelengths between 1 cm and 25 cm are extensively used for RADAR missions and remaining wavelength range is used for telecommunications. In order to avoid interference with radar and telecommunication activities, which also operate in this region, most commercial and domestic microwave ovens operate at 2450 MHz (12.25cm). The difference between microwave energy and other forms of radiation, such as X- and γ -rays, is that microwave energy is non-ionizing and therefore does not alter the molecular structure of the compounds being heated – it provides only thermal activation. The heating effect utilized in microwave assisted organic transformations is mainly due to dielectric polarization. When a molecule is irradiated with microwaves, it aligns itself with the applied field. The rapidly changing electric field (2.45 x 10⁹ Hz) affects the molecule and consequently the molecule continually attempts to align itself with the changing field and energy is absorbed¹. The ability of a material to convert electromagnetic energy into thermal energy is dependent on the dielectric constant. The larger the dielectric constant the greater is the coupling with microwaves. Thus, solvents such as water, methanol, DMF, ethyl acetate, acetone, acetic acid, etc. are all heated rapidly when irradiated with microwaves. However, solvents with low dielectric constants such as hexane, toluene, carbon tetrachloride, etc. do not couple and therefore do not heat that rapidly under microwave irradiation. Microwave heating has thus been found to be a very convenient thermal source not only in the kitchen but also in a chemical laboratory. Chemists have explored the possibility of the application of a

conventional microwave oven to carry out chemical reactions. It has been found that many reactions progress much faster upon microwave irradiation than with traditional heating techniques¹. The application of microwave irradiation to activate and accelerate organic reactions has taken a new dimension and has experienced exponential growth in the last ten years²⁻⁸. Microwave chemistry is becoming increasingly popular both in industry and in academia^{1, 9-13}. We hope to demonstrate in this article the utility of this technique, to prepare new class of pyridone azo dyes and studying their printing properties.

Material and Methods

Materials: The following materials were employed in the study reported here.

Fabric: Polyester (PE) knitted fabric of 150g/m², supplied by a private sector company, was treated with a solution containing 1g/l non-ionic detergent at 70 °C for 1/2 h., thoroughly washed, and air dried at room temperature.

Thickener: Commercial synthetic thickener (Lecuo print) supplied by BASF Company.

Chemicals: 2,4-dimethoxyaniline, 4-methoxyaniline, 4-methylaniline, p-chloroaniline, p-nitroaniline, o-chloro-p-nitroaniline, p-Bromoaniline, 2,4-dichloroaniline, sodium acetate, ethanol, sodium ethoxide, cyanoacetamide, diethylmalonate, hydrochloric acid. All chemical used were in Reagent Grades.

Synthesis: Synthesis of 4-chlorophenylmalonamide General procedure for Microwave irradiation: 4-chloroaniline (10mmol), diethylmalonate (5mmol) were probably mixed in 25ml beaker, the obtained mixture was irradiated in microwave

oven (MICRO-CHEF FM 3935QT) at the power of 1500 w for 2 min., after the irradiation, the crude product was re-crystallized in ethanol .

General procedure for Conventional heating: Mixture of 4-chloroaniline(10mmol), diethylmalonate (5mmol)were refluxed for 4h. and then allowed to cool room temperature. The resulting solid product was collected by filtration. The crude product was re-crystallized in ethanol

Synthesis of 5-arylaazo3-cyano-4,6-dianalinopyridine-2(1H)one derivatives: General procedure for Conventional heating: A mixture of arylazo 4-chlorophenylmalonamide (1,3-dianilino-1,3-propanedione) (0.01mole) **2** and cyanoacetamide **1**(0.01 mole) were dissolved in ethanol (30ml)containing sodium ethoxide (0.01 mole). The mixture was refluxed for 4 h and then allowed to cool room temperature and acidified with dilute hydrochloric acid. The resulting solid product was collected by filtration and crystallized from the ethanol.

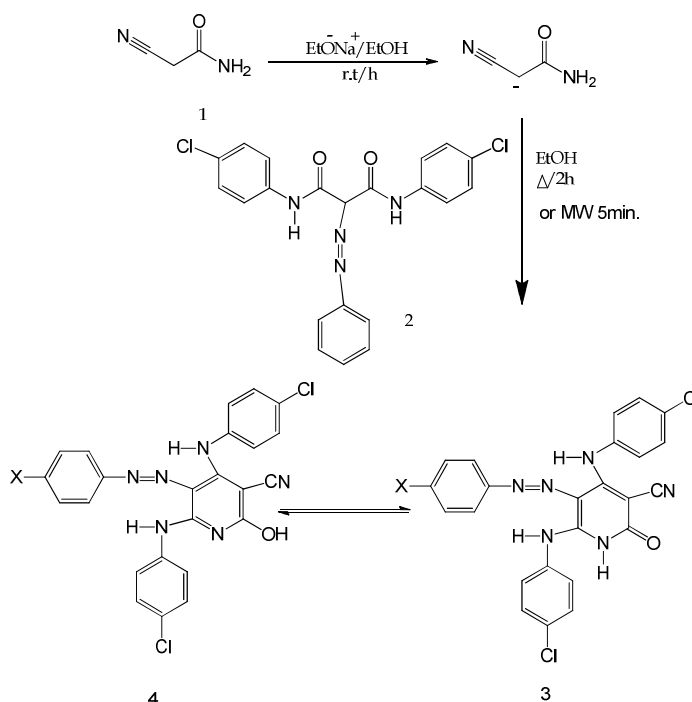
General procedure for Microwave irradiation: A mixture of arylazo 4-chlorophenylmalonamide (1,3-dianilino-1,3-propanedione) (0.01mole) **2** and cyanoacetamide **1**(0.01 mole) were dissolved in ethanol (30ml)containing sodium ethoxide (0.01 mole). The mixture was irradiated in microwave oven at the power of 1500 w for 5 min., and then allowed to cool room temperature and acidified with dilute hydrochloric acid. The resulting solid product was collected by filtration and crystallized from the ethanol scheme 1.

Printing experiment: Lab scale printing experiments were carried out on polyester fabric using the produced dyes. The printing paste 100 gm. consists of 3gm. of sodium alginate as thickener, 3 g. of prepared dye and 96 ml of water. Samples of polyester fabric were silk screen printed using the above printing paste, the printed fabric was dried and fixed at different temperatures 150, 170, 190 and 210°C , fixation time 2 and 3 min. respectively, then washed twice by cold water, then twice with hot water and finally rinsed with cold water, then air dried.

Measurements: Melting point: All melting points of the synthesized dyes were determined in open glass capillaries on gallenkamp melting point apparatus and are uncorrected.

Spectroscopic analyses: The infrared of the synthesized dyes was measured by a Perkin Elmer/1650.FT-IR instrument The ¹H – NMR spectra were measured in a varian 400 or wilmad 270 MHZ spectrometer for (CD₃) SO solutions using SiMe₄ as internal standard. Mass spectra were measured on a Varian MAT CH-5 spectrometer (70 eV). Mass spectra were recorded on a Varian MAT112 spectrometer. Analytical data was obtained from the micro analytical data centre at Cairo University.

Spectrophotometric measurements: The absorbance of the dyes was measured in the ultraviolet-visible region between 300-700 nm by a UNICAM UV spectrophotometer using a 1cm. quartz cell. The dyes were dissolved in absolute ethanol at a concentration of 10⁻⁴ mole/l.



Scheme-1
Structure of synthesized compounds

Colour strength measurements: The reflectance values of the fabric were measured using a Data Colour SF 600+. Relative colour strengths (K/S values) were determined using the Kubelka-Munk equation^{14,15}.
 $K/S = (1-R) / 2R$

Fastness properties measurements: Fastness to washing, rubbing, light and perspiration were assessed according to standard methods¹⁶⁻¹⁸.

Results and Discussion

4-chlorophenylmalonamide was prepared by refluxing 4-chloroaniline (10mmol), diethylmalonate (5mmol) for 4h and 5-arylo3-cyano-4,6-bis(4chlorophenyl)aminopyridine-2(1H)one derivatives were prepared by refluxing substituted arylo3-chloromalonamide with cyanoactamide in the presence of sodium ethoxide in ethanol. The same reactions could be carried out under microwave conditions. It is noteworthy that the reaction which required 4h in conventional method was completed efficiently, with high yield 85% in 2-5 min under microwave conditions table 1. Therefore, microwave procedure could offer an efficient pathway to synthesis 4-chlorophenylmalonamide and 5-arylo3-cyano-4,6-dianilino3-pyridine-2(1H)one derivatives. The microwave technique has been employed to reduce the reaction time, rate enhancement and increase the selectivity and yield.

All the synthesized compounds have been characterized on basis of their element analysis and spectral data (MS, ¹H NMR IR,). The analytical data for 4a revealed a molecular formula C₂₅H₁₈ Cl₂N₄SO (M⁺ = 498), ¹H NMR exhibited broad peak at 11.35(1H, OH), multiple at 6.5-7.79 for aromatic, The IR spectra showed strong broad absorption band at 3500-3150 cm⁻¹ for the hydroxyl (OH) and amide group (NH) and strong sharp band at 2219cm⁻¹ (CN) group table 2 and 3.

The effect of the structural configuration on the UV-visible absorption maxima of the synthesised dyes: The electronic absorption spectra of the synthesised dyes have been studied. Thus the UV spectra of 5-arylo3-cyano-4,6-bis(4chlorophenyl)aminopyridine-2(1H)one derivatives lie in the range 395 – 480 nm table 4. These dyes have two tautomeric formula (enol form) I and (keto form) II. Tautomer I has two resonating structures A and B, scheme 2. Optimum conjugation is observed in the resonating system B, where the lone pair electron of the (OH) group interacts efficiently with arylo3 moiety. Consequently, such a high energy dipolar arrangement will be stabilised when X is an electron- withdrawing group. cyano group in the third position had no shift in absorption. The bathochromic shift is observed in case of dye 4_h and this may be attributed to its molecular structure which possess electron two withdrawing groups (Cl and NO₂ groups).

Colour characteristics of printed polyester: The colour characteristics of printed polyester were investigated and are shown in table (4). It is clear from the table that the colour characteristics of the printed polyester fabric (which expressed as K/S) varied due to difference in the nature of substituents attached to arylo3 moiety of the dye molecules., for ex dye no. 4_h possess high colour strength and this may be attributed to presence of two electron withdrawing groups (Cl, NO₂). The printed polyester samples using the prepared dyes 4_{a-h} were thermo fixed at different temperatures 150, 170, 190 and 210 °C, the fixation time is two and three minutes figures, 1 and 2. The fixation temperature play an important role on the colour strength It is shown from figure 1and 2 that as the fixation temperature increase the colour strength increase over all the dyes. The fixation time 3 min. has no significant effect on the colour strength value.

Table-1
Comparison between Reaction time, Yield % of the synthesized dyes 4_{a-h} using Microwave and Convention heating

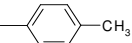
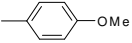
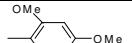
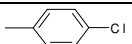
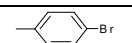
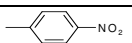
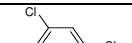
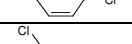
Dye No.	Ar	Reaction time		Yield %	
		Microwave /min	Convention heating	microwave	Convention heating
4 _a		3 min	4h.	65	82
4 _b		3 min	4h.	67	80
4 _c		4 min	5h.	58	80
4 _d		4 min	4h.	60	85
4 _e		4 min	4h.	65	85
4 _f		4	4	66	82
4 _g		5	5	55	82
4 _h		5	5	62	85

Table-2
Physical and analytical data of synthesized dyes 4_{a-h}

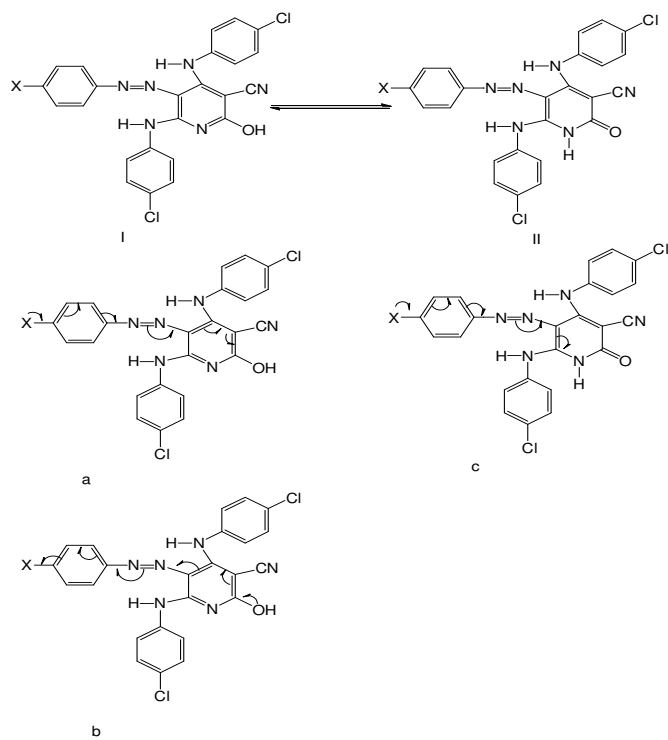
Compound No.	Colour	Yield %	m.p °C	Molecular Formula	Molecular weight	λ max	FT-IR (KBr, ν Cm ⁻¹)		Element analysis							
							Required (%)				Found (%)					
							NH, OH	CN	C	H	N	O	C	H	N	O
4 _a	yellow	84	287	C ₂₅ H ₁₈ Cl ₂ N ₆ O	498	395	3150-3500	2219	61.36	3.71	17.17	3.27	61.09	3.44	17.15	3.11
4 _b	yellow	89	257	C ₂₅ H ₁₈ Cl ₂ N ₆ O ₂	505	416	3150-3500	2216	59.42	3.59	16.63	6.33	59.33	3.40	16.50	6.10
4 _c	orange	85	252	C ₂₆ H ₂₀ Cl ₂ N ₆ O ₃	535	422	3150-3500	2217	58.33	3.77	15.7	8.97	58.11	3.61	15.51	8.81
4 _d	yellow	89	292	C ₂₄ H ₁₅ Cl ₃ N ₆ O	509	430	3150-3500	2217	56.55	2.97	16.49	3.14	56.48	2.88	16.35	3.10
4 _e	orange	88	253	C ₂₄ H ₁₅ BrCl ₂ N ₆ O	554	444	3150-3500	2220	52.97	2.59	15.16	2.89	52.11	2.47	15.09	2.51
4 _f	brown	87	269	C ₂₄ H ₁₅ Cl ₂ N ₇ O ₃	520	460	3150-3500	2216	55.4	2.91	18.84	9.22	55.32	2.85	18.81	2.88
4 _g	brown	85	285	C ₂₄ H ₁₄ Cl ₄ N ₆ O	544	472	3150-3500	2217	52.97	2.59	15.44	2.94	52.88	2.49	15.41	2.88
4 _h	Brown	91	277	C ₂₄ H ₁₄ ClN ₇ O ₃	554	480	3150-3500	2216	51.96	2.54	17.67	8.65	51.45	2.44	17.50	8.59

Table-3
¹H-NMR and mass spectra of the synthesized dyes 4_{a-h}

MS (M ⁺)	¹ H-NMR (ppm.)	Compound no.
488	2.34 (s, 3H, CH ₃), 6.5-8.79(m, 12H, 3 C ₆ H ₄), 4 (s, 2H, 2NH), 11.53 (s, 1H, OH).	4 _a
504	2.5 (s, 3H, OCH ₃), 7.1-8.3 (m, 12H, 3 C ₆ H ₅), 4 (s, 2H, 2NH), 11.4(s,1H, OH).	4 _b
534	3.83 (s, 6H, 2OCH ₃), 6.88-7.77 (m, 11H, 2 C ₆ H ₄ , C ₆ H ₃), 4.2 (s,2H, 2NH), 11.8 (s, 1H, OH).	4 _c
508	6.6-7.78 (m, 12H, 3 C ₆ H ₄), 4 (s, 2H, 2NH), 11.7 (s, 1H, OH).	4 _d
553	7.0-8.2 (m, 12H, 3C ₆ H ₄), 4.4 (s, 2H, 2NH), 11.53 (s, 1H, SH).	4 _e
519	7.2-8.2(m, 12H, 3C ₆ H ₄), 4.2 (s, 2H, 2NH), 11.52 (s, 1H, OH).	4 _f
542	7.24-8.78(m, 11H, 2C ₆ H ₄ , C ₆ H ₃), 4.0 (s, 2H, 2NH), 11.54 (s, 1H, OH).	4 _g
553	7.24-8.35(m, 11H, 2C ₆ H ₄ , C ₆ H ₃), 4.1 (s, 2H, 2NH), 11.61 (s, 1H, OH).	4 _h

Table-4
Colour strength and fastness properties of Screen printed *polyester fabric, using the synthesized dyes (4_{a-h})

Light fastness	Perspiration				Rubbing		Washing		K/S	Dye No.
	Alkali		Acidic		wet	dry	St.	Alt.		
	St.	Alt.	St.	Alt.						
5	5	4	4	5	4	4	4	4	8.5	4 _a
5	4-5	4-5	4	5	4	4	4	4	8	4 _b
5	5	4	5	5	4	4	4	4	7.5	4 _c
5	4-5	5	4	5	4	4	4	4	7.4	4 _d
5-6	5	5	5	5	4-5	5-	4	4	7	4 _e
5-6	5	4	5	5	4	4	4	4	8.2	4 _f
6	4-5	5	4-5	5	4	4	4	4	11	4 _g
6-7	5	5	5	5	4-5	4-5	4	4	11.2	4 _h



Scheme-2

Resonating structure of synthesized compounds

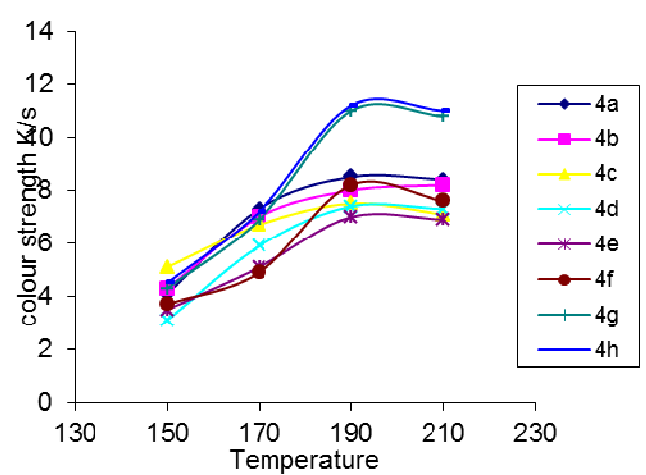


Figure-1

Effect of fixation temperature on the colour strength of silk screen printed polyester using synthesized dyes 4_{a-h}, fixation time 2 min.

Fastness properties: Table 4 showed the fastness properties of screen printed polyester.

Wash fastness: The rate of movement of dye out of the fibre during washing depends on the molecular size of the dye molecules, the type of the linkage between the dye and the fibre and charge located on the dye which in turn, depends the electron donating and electron withdrawing character of the substituents^{19, 20}. The result of wash fastness for printed polyester fabric at 190 °C was 4-5 for most dyes.

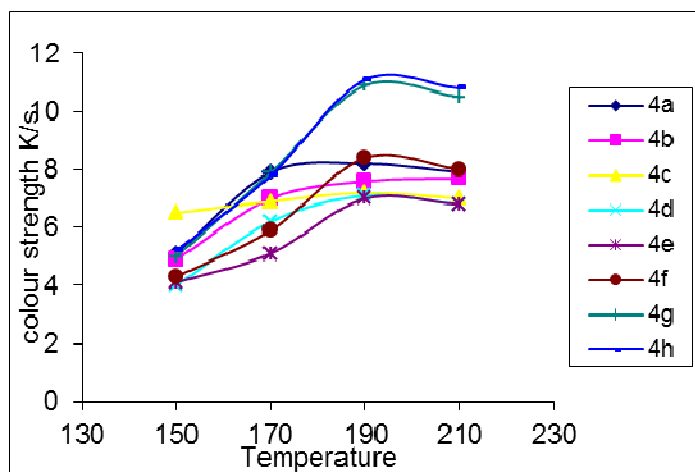


Figure-2

Effect of fixation temperature on the colour strength of silk screen printed polyester using synthesized dyes 4_{a-h}, fixation time 3 min

Perspiration fastness: The magnitude of the dye removal from polyester fabric of perspiration solutions (alkali and acidic) are shown. The result indicates that the dye removal could be dependent on the molecular weight of the dye and the binding forces between the dye and the fibre. Thus dye 4_e and 4_h having higher molecular weight compared to other synthesized dyes, had higher fastness in perspiration solution.

Rub-fastness: A numerical measure for the removal of loosely adhered dye molecules from the fibre surface was achieved through the rubbing test method. The data obtained show higher values of rubbing fastness for dyes of higher molecular weights. Thus dye 4_e and 4_h have rubbing fastness between 4 and 5

Light fastness: Some studies have showed that, anthraquinone dyes are generally more light fast than their counterparts, the light fastness of these dyes arises from their ability to undergo intramolecular proton transfer from OH group to adjacent C=O group following light absorption in the UV region. This is internal conversion process, as the absorbed UV light energy is dissipated as harmless heat. Small no. of light fast azo disperse dyes take advantage of inter molecular hydrogen bond between the azo (N=N) group and adjacent (NH) group to stabilize the dye against UV light degradation, so the good light fastness of our prepared dyes may be arise from their ability to undergo intermolecular hydrogen bond between the azo (N=N) group and adjacent (NH) group²¹.

Conclusion

New derivatives of 5-aryloxy-cyano-4,6-bis(4chlorophenyl)aminopyridine-2(1H)one were synthesized using assistance of microwave technique to reduce the reaction time and produce a good yield. The structure of substituted 5-aryloxyaminopyridine-2(1H)one dyes were established and confirm

for the reaction products on the basis of their element analysis and IR, ¹H-NMR and mass spectra spectra. The substituents on the arylazo moiety of the synthesized dyes have a considerable effect on the colour strength value. This depends on the electron mobility through the resonating system, which in turn depends on the type of the substituent. The printing characteristics of prepared dyes system 4_{a-h} on polyester fabric have good colour strength, good washing, rubbing, perspiration and light fastness.

Acknowledgement

This work was supported by National Research centre, textile division, dyeing, printing and auxiliaries department

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