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Arylazoazines and arylazoazoles as interesting disperse dyes: Recent developments with emphasis on our contribution laboratory outcomes

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REVIEW INFORMATION



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Disperse dyes Arylazoazoles Arylazoazines Polyester fabrics Biological activity Microwave irradiation

1. Introduction

Arylazoazines have replaced arylazopyrazoles as disperse monoazo dyes of superior properties. Among these dyes (1-4) are commercially available (Figure 1) [1-5]. In recent years, we have placed emphasis on developing efficient syntheses of new substitutes aryl and heteroarylazoazines and azoles as potential antimicrobial dyes emphasizing on utility of green methodologies whenever this was possible. In the following article, we survey these results as well as some recent related work worldwide.

This study aims to shed light on the potential of arylazonicotinate, pyrido[3,2,c]cinnolines, pyrido[2,3-d]pyrimidinones, arylazopyridones, arylazothienopyridones, arylazothienopyridazines, arylazopyrazoles and pyrazolopyrimidines as antimicrobial disperse dyes for hydrophobic fibers. Thus, encouraging developing large scale preparations of these products as well as commercial utility in dyeing fabrics having antimicrobial activity.

2. Synthetic approaches to arylazonicotinate, pyrido[3,2,c] cinnolines and pyrido[2,3-*d*]pyrimidinones derivatives

In 1999, Elnagdi *et al.* [6] reported that coupling enaminones, **1**, with aromatic diazonium salts affords arylhydrazonals, **2**, that subsequently condensed with active methylene nitriles to yield pyridazine imines, **3** [7]. However,

with the help of X-ray crystal structure determination as well as ¹³C NMR data it was realized that the reaction of condensing compound 2 with active methylene nitriles produces either pyridazinones or arylazonicotinates based on the reaction conditions [8,9]. It is believed that the pathways for these processes involve initial reaction of compound 2 with active methylene nitriles to yield the hydrazono-enone, 4, that then cyclizes to generate the pyran-imine, 5. In the absence of ammonium ion, compound 5 undergoes a Dimroth type rearrangement to yield compound 7 (Scheme 1) (Table 1) [10,11]. Subsequently, Al-Mousawi et al. has found that in presence excess amount of ammonium acetate the amino derivative 9 is formed. In case of presence excess amount of ammonium acetate pyran-imine, $\mathbf{5}$, is attacked by NH₃ ion yielding acyclic amidine 8 that then cyclizes followed by water elimination to yield compound 9 [11-13]. Previously, it was noted in the literature that in some cases pyridazinones 10 are the reaction products (Figure 2-4) [14-19].

In contrast, 3-oxo-3-substituted-2-arylhydrazonals react with active methylene nitriles to afford the novel 2,6-dihydropyrido[3,2,c]cinnolines, **12**. These substances are believed to be formed via a 6π -electrocyclization reaction of the initially formed arylazo nicotinate **7**, that generates the tricyclic intermediate product **11**, which then aromatizes to produce the cinnoline derivatives, **12** (Scheme 2) [9,11,12].

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ABSTRACT

In this review, we report a survey on the synthesis and application of arylazoazines and arylazoazoles as versatile disperse dyes. Recent reports on the synthesis of arylazonicotinates via condensing arylhydrazonals with active methylene nitriles in acetic acid in presence of ammonium acetate is surveyed. The scope and limitations of this synthetic approach which in some cases afford pyridazinones or arylazonicotinates is defined. Microwave assisted as well as ultra sound assisted synthesis of arylazopyridones as established marketed dyes is also surveyed. Conversion of these arylazopyridones into arylazothienopyridones that can de converted into arylazoinoline derivatives is discussed. Synthesis of arylazopyrazoles and pyrazolopyrimidines via microwave or ultra sound is discussed. The utility of the synthesized compounds as well as antimicrobial disperse dyes and efforts to define their potentialities are also covered.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Compound	R	Ar	Х	M.p. (°C)	Yield (%)
3b Thien-2yl $CHANO_2p$ CO_2Et $170-172$ 67 3c $Fur-2yl$ $CHANO_2p$ CO_2Et $124-2244$ 75 7a $CAHs$ $CHANO_2p$ CO_2Et $124-2244$ 75 7a $CAHs$ $CAHCH_3p$ $CONH_2$ $276-273$ 85 7c $CAHsANO_2p$ $CAHs$ CNH_2 3300 74 7c $CHASPP$ $CAHs$ CNH_2 3300 74 7c CH_3 $CAHs$ CSH_2 3300 74 7c CH_3 $CAHs$ CSH_2 3300 74 7f CH_3 CH_5 CNH_2 3300 74 7f CH_3 CH_5 $CONH_2$ 3300 74 7f CH_3 CH_5 $CONH_2$ 3300 74 7f CH_3 CH_5 $CONH_2$ 3300 75 7f CH_4 CH_5 $CONH_5$ CN_5 75 71 190 96 75 7	3a	C ₆ H ₅	C ₆ H ₄ NO ₂ -p	CO ₂ Et	199-201	74
3c Fur-2-yl CH,NO ₂ p CO ₂ Et 242-244 75 7a CdHs CH,NO ₂ p CO ₂ Et 180-182 84 7b CdH CH,CH ₂ p CO ₂ Et 180-182 84 7c CdH,NO ₂ p CdH,CH ₂ p CONH ₂ 276-277 85 7c CdH,NO ₂ p CdH CN 276-277 85 7d CdH,CH ₂ p CdH CN 276-277 85 7d CdH,S CN 156-168 72 7e CH CdH CN 153 95 7f CdH CdH CH 5300 74 7g CdH CdH CH 53 95 7h CdH CdH CH 53 95 7h CdH,S CSNH2 190 98 7h CdH,S CSNH2 188-190 87 7h CdH,CH-p.p CdH CN 145 95 7h CdH CdH CN 145 95	3b	Thien-2-yl	C ₆ H ₄ NO ₂ -p	CO ₂ Et	170-172	67
7a CHS CH4(Hsp) CO-Bt 180-182 84 7b C.Hs CH4(Hsp) CONH; 276-277 85 7c C.Hs C.Ha(Hsp) C.Hs 276-277 85 7d C.Hs C.Ha(Hsp) C.Hs 276-277 85 7d C.Hs C.Hs C.NH2 300 74 7e C.Hs C.AHs CONH2 >300 95 7f C.Hs C.AHs CONH2 >300 95 7g C.Hs C.AHs CONH2 >300 95 7h C.Hs C.AHs CONH2 >300 95 7h C.Hs C.AHs CONH2 >300 95 7h C.Hs C.AHs CONH2 188-190 87 7h C.Hs C.AHs CONNH2 237 95 7h C.Hs C.AHs CONNH12 237 95 7h M.A.CHSP.p C.AHs CONNH12 237 95 7h C.Hs C.AHs CONNH	3c	Fur-2-yl	$C_6H_4NO_2-p$	CO ₂ Et	242-244	75
7b CHs CH4CHs-p CONH2 276-278 85 7c CH4NO ₂ p CH4 CN 276-278 85 7d CH4O ₂ p CAH5 CSNH2 166-168 72 7e CH5 CAH5 CSNH2 166-168 72 7e CH5 CAH5 CSNH2 300 74 7f CH5 CAH5 CONH2 >300 74 7g CH5 CAH5 CONH2 >300 74 7h CH5 CAH5 CONH2 >300 74 7h CH5 CAH5 CONH2 >300 95 7h CH5 CAH5 CONH2 188-190 87 7h CH5 CAH5 CONH112 237 95 7h CH5 CH5 CN12 242 98 7h Thien-2-yl CH5 CN15 192-195 89 7h Thien-2-yl CH5 CO2Et 192-195 89 7h CH2-Cl-p CAH5 CO2Et 1	7a	C ₆ H ₅	C ₆ H ₄ CH ₃ -p	CO ₂ Et	180-182	84
7c CdH M0:p CdHs CN 276-278 85 7d CdH CH:p CdHs CSNH; 166-168 72 7e CHs CdHs CONH; 3300 74 7f CdHs CdHs CONH; 3300 74 7g CdHs CdHs CONH; 153 95 7n CdHs CdHs CONH; 190 98 7h CdHs CdHs CSNH; 190 98 7h CdHs CdHs CSNH; 190 98 7h CdHs CdHs CSNH; 190 98 7h CdHs CdHs CN 145 95 7h CdHs CdHs CONHH; 237 95 7h CdHs CoHs CN 214 95 7n Fur-2-yl CdHs CONH 1415 95 7n CdHsOH*p CdHs CopEt 193-195 89 7n CdHsOH*p CdHs CopEt 193-195 <	7b	C ₆ H ₅	C ₆ H ₄ CH ₃ -p	CONH ₂	276-277	85
7d CaH, Chr.p CaHs CMHz 166-168 72 7e CH3 CaHs CONHz >300 74 7f CaHs CaHs 2300 95 7g CaHs CaHs 2300 95 7h CaHs CaHs CN 153 95 7h CaHs CaHs COPt 188-190 87 71 CaHs CaHs CON 145 95 7h CaHs CaHs CN 145 95 7h CaHs CaHs CN 145 95 7h CaHs CAHs CN 242 98 7h Thien2-yl CaHs CN 214 95 7n Fur-2-yl CaHs COpEt 193-195 89 7n CaHsOHr-pp CaHs COpEt 193-195 89 7a CaHsOHr-pp CaHs COpEt 193-195 89 7a Pyrroi-2-yl CaHs CopEt 188-190 68 <	7c	$C_6H_4NO_2-p$	C ₆ H ₅	CN	276-278	85
7e CH3 CH3 CH4; CONH2 >300 74 7f CH5 CH5 μ_{μ} >300 95 7g CH5 CH5 CH5 μ_{μ} >300 95 7h CH5 CH5 CN 153 95 7h CH5 CH5 CN 153 95 7h CH5 CH5 CN 190 98 71 CH5 CH5 CN 145 95 7k CH5P-p CH5 CONHN12 237 95 7k CH3CHP CH5 CONHN12 237 95 7n CH3CHp CH5 CONHN12 237 95 7n CH3CHp CH5 CONHN12 237 95 7n CH3CHp CH5 CO2Et 174-176 75 7p Purol-2-yl CH5 CO2Et 174-176 75 7p Pyrol-2-2yl CH5 CO2Et 202-204 60 7r CH3C CO2Et 210-212 </td <td>7d</td> <td>C₆H₄CH₃-p</td> <td>C₆H₅</td> <td>CSNH₂</td> <td>166-168</td> <td>72</td>	7d	C ₆ H ₄ CH ₃ -p	C ₆ H ₅	CSNH ₂	166-168	72
7f CdHs CdHs CdHs 300 95 7g CdHs CdHs CN 153 95 7h CdHs CdHs COPEt 188-190 87 71 CdHsPhp CdHs COPEt 188-190 87 71 CdHsPhp CdHs CN 145 95 7k CdHsPhp CdHs CN 145 95 7h CdHsPhp CdHs CN 145 95 7h CdHsCP CdHs CN 214 95 7n CdHsCP CdHs COPEt 174-176 75 7p Pyrrol-2-yl CdHs COPEt 202-204 60 7q Pyrazin-2-yl CdHs COPEt 202-204 60 7q Pyrazin-2-yl CdHs COPEt 202-204 60 7q Pyrazin-2-yl CdHs COPEt 200-202 80 7r CdHs COPEt 200-202 80 96 9b CdHs COPEt 18	7e	CH ₃	C ₆ H ₅	CONH ₂	>300	74
7gCoHsCoHsCoHsCN153957hCoHsCoHsCOEt188-190877iCoHsCoHsCOEt188-190987jCoHsCoHsCNN145957kCoHsPh-pCoHsCONH12237957kCoHsPh-pCoHsCONHNH2237957kCoHsPh-pCoHsCONHNH2237957kCoHsPh-pCoHsCONHNH2237957nCoHsCCoPet193-195897nCoHsCCoPet174-176757pPyrcol-2-ylCoHsCO2Et202-204607qPyrazin-2-ylCoHsCCo2Et202-204607qPyrcol-2-ylCoHsCCo2Et202-204607eCoHsCCo2Et202-20460687rCoHsCo2Et202-20460687rCoHsCo2Et188-19056567rCoHsCo2Et210-212819aCoHsCoHsCo2Et210-212809cCoHsCo4HsCh-pCo2Et188-190569dOpetCoHsCo2Et188-190689dNaphtalene-2-ylCoHsCO2Et188-1905510bCoHsCh-pCo2Et108-1105510bCoHsCh-pCo2Et108-1886410dCoHsCh-pCo2Et <t< td=""><td>7f</td><td>C₆H₅</td><td>C₆H₅</td><td>ş–</td><td>>300</td><td>95</td></t<>	7f	C ₆ H ₅	C ₆ H ₅	ş–	>300	95
7g CaHs CaHs CaHs Construction 153 95 7h CaHs CaHs Construction 198-190 87 7i CaHs CaHs Construction 190 98 7i CaHsPh-p CaHs CNH2 190 98 7i CaHsPh-p CaHs CNH2 237 95 7k CaHsPh-p CaHs CONNNH2 237 95 7m Fur-2-yl CaHs CONNNH2 242 98 7m Fur-2-yl CaHs CONEN 242 98 7m Fur-2-yl CaHs COpEt 193-195 89 7o CaHsOLP CaHs COpEt 202-204 60 7q Pyrazin-2-yl CaHs CoEt 202-204 60 7q Pyrazin-2-yl CaHs CoEt 200-202 80 7r GaHs CaHaCHs-p CoEt 200-202 80 92 CaHs CaHaCHs-p CoEt 200-202 80 94 </td <td></td> <td></td> <td></td> <td>∕~_N∕≂o</td> <td></td> <td></td>				∕~ _N ∕≂o		
Th CdHs CdHs CdHs CoEt 188-190 87 71 CdHs CdHs CSNH2 190 98 71 CdHsPrp CdHs CNN 145 95 7k CdHsPrp CdHs CONHNH2 237 95 7l Thien-2-yl CdHs CONHNH2 242 98 7m Fur-2-yl CdHs CO_Et 193-195 89 7n CdHsOH3-p CdHs CO_Et 193-195 89 7o CdHsOH3-p CdHs CO_Et 193-195 89 7o CdHsOH3-p Colst 193-195 89 7o CdHsOH3-p Colst 174-176 75 7p Pyrozin-2-yl CdHs CO_2Et 202-204 60 7r $furtheater CdHs Colet 200-202 80 7r furtheater CdHs Colet 200-202 80 9a CdHs CdHs Colet 188-190 68 9b CdHs CHs$	7g	C ₆ H ₅	C ₆ H ₅	CN	153	95
7i Ch b Ch b CSNH2 190 98 7j $C_{0}H_{5}Pr-p$ $C_{0}H_{5}$ CN 145 95 7k $C_{0}H_{5}Pr-p$ $C_{0}H_{5}$ CONHNH2 237 95 7l Thien-2-yl $C_{0}H_{5}$ CONHNH2 242 98 7m Fur-2-yl $C_{0}H_{5}$ CN 214 95 7n $C_{1}H_{5}Clrp$ $C_{1}H_{5}$ CO2Et 193-195 89 7o $C_{1}H_{5}Clrp$ $C_{1}H_{5}$ CO2Et 174-176 75 7p Pyrozin-2-yl $C_{1}H_{5}$ CO2Et 202-204 60 7q Pyrazin-2-yl $C_{1}H_{5}$ CO2Et 300 68 7r $\int_{0}^{-1} \int_{0}^{-1} \int_{0}$	7h	C ₆ H ₅	C ₆ H ₅	CO ₂ Et	188-190	87
$7j$ $C_{H1}^{h}p^{p}$ $C_{H1}^{h}s$ CN 145 95 $7k$ $C_{AH5}^{h}p^{p}$ $C_{AH5}^{h}s$ $CONHNH_{2}$ 237 95 $7l$ Thien-2-yl $C_{AH5}^{h}s$ $CONHNH_{2}$ 242 98 $7m$ $Fur-2-yl$ $C_{6H5}^{h}s$ CN 214 95 $7n$ $C_{AH,CH1-p}$ $C_{AH5}^{h}s$ $CO_{2}Et$ 193.195 89 $7o$ $C_{AH,CH1-p}$ $C_{AH5}^{h}s$ $CO_{2}Et$ 174.176 75 $7p$ Pyrrol-2-yl $C_{AH5}^{h}s$ $CO_{2}Et$ 202.204 60 $7q$ Pyrazin-2-yl $C_{AH5}^{h}s$ $CO_{2}Et$ 202.204 60 $7r$ $\int_{q} \int_{q} \int_$	7i	C ₆ H ₅	C ₆ H ₅	CSNH ₂	190	98
7k CeHsPh-p CeHs CONHNH2 237 95 71 Then-2-yl CeHs μ_{1} 242 98 7m Fur-2-yl CeHs CN 214 95 7m CeHsCP-p CeHs CONHNH2 214 95 7m CeHsCP-p CeHs CO2Et 193-195 89 7o CeHsOCH3-p CeHs CO2Et 174-176 75 7p Pyrrol-2-yl CeHs CO2Et 202-204 60 7q Pyrazin-2-yl CeHsCH3-p CO2Et >300 68 7r $++$ CeHs Co2Et 210-212 81 9a CeHs Co4HsCH3-p CO2Et 200-202 80 9c CeHs Co4HsCl-p CO2Et 200-202 80 9c CeHs CeHsCl-p CO2Et 188-190 68 9d Naphthalene-2-yl CeHsCl-p CO2Et 89-90 77 10a CeHsCH3-p CeHs CO2Et 108-110 55 <td< td=""><td>7j</td><td>C₆H₅Ph-p</td><td>C₆H₅</td><td>CN</td><td>145</td><td>95</td></td<>	7j	C ₆ H ₅ Ph-p	C ₆ H ₅	CN	145	95
71 Thien-2-yl C_6H_5 $\Box + c_{1} + c_{2} + c_{2} + c_{3} + c_{4} + c_{5} + c_{5} + c_{4} + c_{5} + c_{5}$	7k	C ₆ H ₅ Ph-p	C ₆ H ₅	CONHNH ₂	237	95
7mFur-2-ylCeH5CN214957nCiH5Cl-pCeH5CO2Et193-195897oCeH4OCH3-pCeH5CO2Et174-176757pPyrrol-2-ylCeH5CO2Et202-204607qPyrazin-2-ylCeH4CH3-pCO2Et300687r $fightarrow equation (Control of the second of t$	71	Thien-2-yl	C ₆ H ₅	N	242	98
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-		s		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7m	Fur-2-yl	C ₆ H ₅	CN	214	95
70 $C_6H_4OCH_3 \cdot p$ C_6H_5 CO_2Et $174 \cdot 176$ 75 7pPyrrol-2-yl C_6H_5 CO_2Et $202 \cdot 204$ 60 7qPyrazin-2-yl $C_6H_4CH_3 \cdot p$ CO_2Et 300 68 7r $\int_{0}^{0} \int_{0}^{1} \int_{0}^{$	7n	C ₆ H ₅ Cl-p	C ₆ H ₅	CO_2Et	193-195	89
7pPyrrol-2-yl C_6H_5 CO_2Et $202-204$ 60 7qPyrazin-2-yl CAH_4CH_3-p CO_2Et >300 68 7r	70	C ₆ H ₄ OCH ₃ -p	C ₆ H ₅	CO ₂ Et	174-176	75
7qPyrazin-2-yl $C_6H_4CH_3-p$ CO_2Et >300687r \downarrow \downarrow C_6H_5 CO_2Et 188-190569a C_6H_5 $C_6H_4CH_3-p$ CO_2Et 210-212819b $C_6H_4NO_2-p$ C_6H_5 CO_2Et 200-202809c C_6H_5 CAH_4CI-p CO_2Et 188-190689dNaphthalene-2-yl C_6H_4CI-p CO_2Et 89-907710a $C_6H_4CH_3-p$ C_6H_5 CO_2Et 108-1105510b $C_6H_4CH_3-p$ C_6H_5 $CONH_2$ 243-2455210c $C_6H_4CH_3-p$ C_6H_5 $CONH_2$ 211-2137012aH $C_6H_4NO_2-p$ CO_2Et 148-1506212bH $C_6H_4NO_2-p$ CO_2Et 143-1488312cH $C_6H_4NO_2-p$ CO_2Et 143-1488312cH C_6H_5 $CONH_2$ 1509812c H_4 C_6H_5 $CONH_2$ 1509812c C_6H_5 C_6H_5 $CONH_2$ 2309012f C_6H_5 C_6H_5 $CSNH_2$ 17095	7p	Pyrrol-2-yl	C ₆ H ₅	CO ₂ Et	202-204	60
7r	7q	Pyrazin-2-yl	C ₆ H ₄ CH ₃ -p	CO ₂ Et	>300	68
9a G_{cH5} $G_{cH4}CH_3 - p$ CO_2Et $210 - 212$ 81 9b $G_{cH4}NO_2 - p$ G_{cH5} CO_2Et $200 - 202$ 80 9c G_{cH5} $G_{cH4}Cl - p$ CO_2Et $200 - 202$ 80 9dNaphthalene - 2 - yl $G_{cH4}Cl - p$ CO_2Et $89 - 90$ 77 10a $G_{cH4}CH_3 - p$ $G_{cH4}Cl - p$ CO_2Et $89 - 90$ 77 10b $G_{cH4}CH_3 - p$ G_{cH5} $CONH2$ $243 - 245$ 52 10c $G_{cH4}CH_3 - p$ G_{cH5} $CONH2$ $243 - 245$ 52 10d $G_{cH4}CH_3 - p$ G_{cH5} $CONH2$ $211 - 213$ 70 12aH $G_{cH4}NO_2 - p$ CO_2Et $148 - 150$ 62 12bH $G_{cH4}Cl - p$ CO_2Et $143 - 148$ 83 12cH G_{cH5} $CONH_2$ 195 82 12dH G_{cH5} $CONH_2$ 150 98 12e G_{cH5} G_{cH5} $CONH_2$ 230 90 12f G_{cH5} G_{cH5} $CSNH_2$ 170 95	7r	0	C ₆ H ₅	CO ₂ Et	188-190	56
9a C_6H_5 $C_6H_4CH_3 \cdot p$ CO_2Et $210 \cdot 212$ 81 9b $C_6H_4NO_2 \cdot p$ C_{AH_5} CO_2Et $200 \cdot 202$ 80 9c C_6H_5 C_02Et $200 \cdot 202$ 80 9c C_6H_5 $C_6H_4Cl \cdot p$ CO_2Et $89 \cdot 90$ 77 10a $C_6H_4CH_3 \cdot p$ $C_6H_4Cl \cdot p$ CO_2Et $89 \cdot 90$ 77 10b $C_6H_4CH_3 \cdot p$ C_6H_5 $CONH_2$ $243 \cdot 245$ 52 10c $C_6H_4CH_3 \cdot p$ C_6H_5 $CONH_2$ $211 \cdot 213$ 70 12aH $C_6H_4Cl \cdot p$ CO_2Et $148 \cdot 150$ 62 12bH $C_6H_4O_2 \cdot p$ CO_2Et $143 \cdot 148$ 83 12cH $C_6H_4O_2 \cdot p$ $CONH_2$ 150 98 12dH C_6H_5 $CONH_2$ 150 98 12e C_6H_5 C_6H_5 $CONH_2$ 230 90 12f C_6H_5 C_6H_5 $CSNH_2$ 170 95		N-CH ₂				
9b $C_6H_4NO_2 \cdot p$ C_6H_5 CO_2Et $200-202$ 80 9c C_cH_5 C_cH_4Cl-p CO_2Et $188-190$ 68 9dNaphthalene-2-yl C_6H_4Cl-p CO_2Et $89-90$ 77 10a $C_6H_4CH_3 \cdot p$ C_6H_5 CO_2Et $89-90$ 55 10b $C_6H_4CH_3 \cdot p$ C_6H_5 $CONH_2$ $243-245$ 52 10c $C_6H_4CH_3 \cdot p$ C_6H_5 CNN $186-188$ 64 10d C_6H_5Cl-p C_6H_5 CNN $186-188$ 64 12aH $C_6H_4NO_2 \cdot p$ CO_2Et $148-150$ 62 12bH $C_6H_4NO_2 \cdot p$ CO_2Et $143-148$ 83 12cH C_6H_5 $CONH_2$ 155 82 12dH C_6H_5 $CONH_2$ 150 98 12e C_6H_5 C_6H_5 $CSNH_2$ 230 90 12f C_6H_5 $CSNH_2$ 170 95	9a	C ₆ H ₅	C ₆ H ₄ CH ₃ -p	CO ₂ Et	210-212	81
9c C_6H_5 C_6H_4Cl-p CO_2Et 188-190689dNaphthalene-2-yl C_4H_4Cl-p CO_2Et 89-907710a $C_6H_4CH_3-p$ C_6H_5 CO_2Et 108-1105510b $C_6H_4CH_3-p$ C_6H_5 $CONH_2$ 243-2455210c $C_6H_4CH_3-p$ C_6H_5 CN 186-1886410d C_6H_5Cl-p C_6H_5 CN 186-1886412aH C_6H_5Cl-p CO_2Et 148-1506212bH C_6H_4Cl-p CO_2Et 143-1488312cH C_6H_5Cl-p $CONH_2$ 1958212dH C_6H_5 CNH_2 1509812dH C_6H_5 $CONH_2$ 2309012e C_6H_5 C_6H_5 $CSNH_2$ 17095	9b	$C_6H_4NO_2-p$	C ₆ H ₅	CO ₂ Et	200-202	80
9dNaphthalene-2-yl C_6H_4Cl-p CO_2Et $89-90$ 77 10a $C_6H_4CH_3-p$ C_6H_5 CO_2Et $108-110$ 55 10b $C_6H_4CH_3-p$ C_6H_5 $CONH_2$ $243-245$ 52 10c $C_6H_4CH_3-p$ C_6H_5 $CONH_2$ $243-245$ 52 10d C_6H_5Cl-p C_6H_5 $CONH_2$ $211-213$ 70 12aH C_6H_4Cl-p CO_2Et $148-150$ 62 12bH C_6H_4Cl-p CO_2Et $143-148$ 83 12cH C_6H_5Cl-p $CONH_2$ 195 82 12dH C_6H_5 $CONH_2$ 150 98 12dH C_6H_5 $CONH_2$ 230 90 12e C_6H_5 C_6H_5 $CSNH_2$ 170 95	9c	C ₆ H ₅	C ₆ H ₄ Cl-p	CO ₂ Et	188-190	68
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9d	Naphthalene-2-yl	C ₆ H ₄ Cl-p	CO ₂ Et	89-90	77
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10a	C ₆ H ₄ CH ₃ -p	C ₆ H ₅	CO ₂ Et	108-110	55
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10b	C ₆ H ₄ CH ₃ -p	C ₆ H ₅	CONH ₂	243-245	52
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10c	C ₆ H ₄ CH ₃ -p	C ₆ H ₅	CN	186-188	64
12a H $C_6H_4N0_2 \cdot p$ CO_2Et 148-150 62 12b H $C_6H_4N0_2 \cdot p$ CO_2Et 143-148 83 12c H $C_6H_4N0_2 \cdot p$ $CONH_2$ 195 82 12d H C_6H_5 $\sum_{h} p_{h}$ 150 98 12e C_6H_5 C_6H_5 $CSNH_2$ 230 90 12f C_6H_5 C_6H_5 $CSNH_2$ 170 95	10d	C ₆ H ₅ Cl-p	C ₆ H ₅	CONH ₂	211-213	70
12b H C_6H_4Cl-p CO_2Et 143-148 83 12c H $C_6H_4NO_2-p$ $CONH_2$ 195 82 12d H C_6H_5 S_{N-Ph} 150 98 12e C_6H_5 C_0H_5 $CONH_2$ 230 90 12f C_6H_5 C_6H_5 $CSNH_2$ 170 95	12a	Н	C ₆ H ₄ NO ₂ -p	CO ₂ Et	148-150	62
12c H $C_6H_4NO_2 \cdot p$ CONH2 195 82 12d H C_6H_5 $\sum_{h \to Ph}$ 150 98 12e C_6H_5 C_0H_5 CONH2 230 90 12f C_6H_5 C_6H_5 $CSNH_2$ 170 95	12b	Н	C ₆ H ₄ Cl-p	CO ₂ Et	143-148	83
12d H C_6H_5 s_{N-ph} 150 98 12e C_6H_5 C_6H_5 $C0NH_2$ 230 90 12f C_6H_5 C_6H_5 $CSNH_2$ 170 95	12c	Н	C ₆ H ₄ NO ₂ -p	CONH ₂	195	82
I2e C6H5 C6H5 ONH2 230 90 12f C6H5 C6H5 CSNH2 170 95	12d	Н	C ₆ H ₅	SPh	150	98
12f C ₆ H ₅ C ₆ H ₅ CSNH ₂ 170 95	12e	C ₆ H ₅	C ₆ H ₅	CONH ₂	230	90
	12f	C ₆ H ₅	C ₆ H ₅	CSNH ₂	170	95

Table 1. Yields of compounds 3, 7, 9, 10 and 12.



1- Greenish Yellow [37781-00-3] [1]



3- C.I. Disperse Yellow 211, 12755 [70528-90-4] [3]



2- C.I. Disperse Yellow 241, 128450 [83249-52-9] [2]



4- Greenish Yellow [88938-37-8] [4]

Figure 1. Examples of some commercially available dyes.

The formed aminonictinates **9a** could be readily converted to ethyl 5-*p*-tolyldiazenyl)-2-(aminomethyleneamino)-6-phenyl nicotinate **13** *via* condensation with *N*,*N*-dimethylformamide dimethylacetal (DMFDMA) in presence of ammonium acetate.

Furthermore, the reaction of compound **13** with ammonium acetate in presence of acetic acid produces

7-phenyl-6-(*p*-tolyldiazenyl)pyrido[2,3-*d*]pyrimidin-4(3*H*)-one, **14** (Scheme 3).

Compounds **7a-e**, **7p**, **7q** and **9a-d** were tested as disperse dyes on polyester fabrics, where **7a-e**, and **9a-c** display yellow to brownish-green hues, in addition with very good washing and perspiration fastness and moderate light fastness [20].



Scheme 1



Figure 2. ORTEP drawing of compound 7a.

While **7p**, **7q** and **9d** display yellowish-orange to dark brown hues, and displayed excellent washing and perspiration fastness and moderate light fastness [21].

The antimicrobial activities of the synthesized dyes were screened against selected bacteria and fungi by the agar well diffusion method and their inhibition zones diameters, given in (Table 2), the tests reveal that all of the tested arylazonicotinates disperse dyes showed positive antimicrobial activities against at least one of the tested microorganisms. All of them showed strong activities (>10 mm inhibition zone) against *Staphylococcus aureus*.



Figure 3. ORTEP drawing of compound 9a.









Figure 4. ORTEP drawing of compound 10a.

Two of the dyes **7a** and **9a**, showed medium activities against Gram negative bacteria. Where most of the dyes showed no activities against the two strains of Gram negative bacteria used in the study.

Also the majority of the dyes showed weak to no activities at all with *Bacillus subtilis*. Only dye **7d** showed significant inhibition zone >10 mm, against *Candida albican*. The other dye that showed medium activities against yeast is **7c** while all the other dyes failed to affect the yeast growth. It is of value to mention here that after six days the inhibition zone did not show any difference in the size, yet the zone is not clear which indicates that the dye **9b** did not kill the microorganisms, but rather had weakened their growth only, this is in comparison to dye **7a** or to ampicillin as reference [20].

Also the inhibition zone diameter data for the disperse dyes **7p**, **7q** and **9d**, given in Table 3, shows that all of the tested dyes showed strong positive antimicrobial activities against at least one of the tested microorganisms. All disperse dyes show strong ability to inhibit the growth of *Candida albicans* which could be considered as interesting observations which needs further investigation. Disperse dye **9d** showed the strongest inhibition zones among the five tested microorganisms, also all of these dyes showed cytotoxic effect even after five days of incubation, there were no growths recorded in the inhibited zone for all five tested microorganisms [21].

3. Synthetic approaches to arylazopyridones and arylazothienopyridones

As has been indicated arylazopyridones are already in the market **1-4** (Figure 1) and are prepared from pyridones **19a-q**. However, in the last decade, we could develop green syntheses of this pyridones utilizing microwave irradiating mixture of acetoacetic esters **15** and cyanoacetamides **16** as well as sonofication of these mixtures.

Dye no	Inhibition zone diameter (Nearest mm) (Mean±SD)							
	B. subtilis	S. aureus	E. coli	P. aeruginosa	C. albicans			
7a	0.1 ± 0.08	15 ± 0.02	77	-	-			
7b	0.7 ± 0.13	16	-	-	7 ± 0.07			
7c	-	11 ± 0.87	-	-	-			
7d	0.1	16 ± 0.08	-	-	12 ± 0.1			
9a	-	13	7	7 ± 0.05	-			
9b	-	10 ± 0.2	-	-	-			
Ampicillin ^b	30 ± 0.05	46 ± 0.7	31 ± 0.14	17 ± 0.07	-			
Cyloheximide ^c					_			

Table 2. Diameter of the zones of inhibition of the dye 7a-e, and 9a,b^a.

a "-": no inhibition, SD: Standard deviation.

^b Ampicillin: Antibacterial (100 mg/mL).

^c Cycloheximide: Antifungal (100 mg/mL).

Cyclonexinnuc. Antinungai (100 mg/ mi

Table 3. Diameter of the zones of inhibition of the dye 7p, 7q and 9d a.

Dye no	Inhibition zone	Inhibition zone diameter (Nearest mm) (Mean±SD)						
	B. subtilis	S. aureus	E. coli	P. aeruginosa	C. albicans			
7р	0.7±0.7	-	2.9±5.8	-	13.4±0.4			
7q	12.4±0.2	12.3±0.3	12.7±0.4	13±0.5	11.6±0.4			
9d	12.7±0.2	11.7±0.4	14.7±0.4	16.1±0.5	12.2±0.2			
Ampicillin ^b	15±1	18.4±3.5	18.6±1.3	16.0±0.5				
Cyloheximide c					-			

a "-": no inhibition, SD: Standard deviation.

^b Ampicillin: Antibacterial (100 mg/mL).

c Cycloheximide: Antifungal (100 mg/mL).

The obtained products and their yields are listed in Table 4. Alternately we could also show what mixtures of acetoacetic esters **15**, cyanoacetic esters **17** and primary amines **18** gives directly the designed pyridones. However in our hands the multistep approach proved superiors since larger yields are obtained in this way. Practically, 1,2-dihydro-6-hydroxy-4methyl-2-oxo-3-pyridine carbonitrile **190** and other 1substituted derivatives have found wide application in the preparation of azo dyes, especially as disperse dyes for synthetic fibres [22-37].

There are many methods for the synthesis of compounds 19a-h. Condensation of methyl acetoacetate with appropriate amines and methyl cyanoacetate is one of the common methods [38,39]. Also basic condensation of N-alkylaceto acetamide with enamino- β -ketoesters lead to 2(1*H*)pyridinones [40]. Another efficient method is heating cyanoacetamide and methyl acetoacetate in a microwave oven [41]. Balalaie et al. [42-48] have reported an efficient three component condensation of alkyl cyanoacetates, primary amines, and β -ketoesters with higher yields on the surface of silica gel, montmorillonite K-10, zeolite, and acidic alumina under microwave irradiation, the obtained products 19a-h in yields ranging from 91 to 93%. These compounds have two tautomeric forms, and in solution there is a very fast equilibration between them [49]. Sakoma et al. [50] has also reported three component condensations of ethyl cyano acetate, primary amines, and ethyl acetoacetate without catalyst. The yields of the obtained products 190-q ranged from 86 to 91%. Pyridones 19a-q could be readily coupled with aromatic and heteroaromatic diazonium salts affording the corresponding aryl and heteroaromatic azopyridones 21a-t (Table 4). Sakoma et al. [50] and Ashkar et al. [51] have evaluated 3-(p-substituted phenylazo)-6-pyridone dyes 21a-d and 21j-t as disperse dyes on polyester fabrics in order to examine the influence of substituent on the color of the prepared dyes. Sakoma et al. concluded that the exhaustion of the dyes was very good on polyester fabric with excellent wash and light fastness properties. These dyes, however, are noteworthy in their excellent affinity and intensity of color. Other outstanding characteristics of these dyes are that they give deep and bright hues with level dyeings. The bright hue might be attributed to the high planarity of the pyridone ring, because of the lower steric interaction of a five membered ring. The remarkable degree of levelness and brightness after washing is indicative of good penetration and the excellent exhaustion of these dyes for the polyester fabric due to the accumulation of polar groups [50].

As anticipated the aryl and heteroaromatic azopyridones **21e-i** reacted with elemental sulphur either under heating with microwave or by using ultra sound or by conventional heating to yield the corresponding aminothienopyridinones **22a-e**. Trials to develop condensed arylazopyridones have been made by Al-Mousawi *et al.* [52] and Al-Zaydi *et al.* [53]. Thus Al-Mousawi reported that reaction of compound **22d** with dimethyl acetylenedicarboxylate afforded arylazoisoquinoline, **24**, while Al-Zaydi *et al.* reported that compound **22e** undergoes cycloaddition to acrylonitrile yielding isoquinolines, **26**. However, up to date, no trial to test potential utility of the isoquinolines **22** and **26** as unique disperse dyes has been made (Scheme 4).

4. Synthetic approaches to arylazothienopyridazines

Other class of arylazoazines has also been synthesized by Al-Mousawi et al. [54-56]. Thus arylazopyridazinone 27 reacted with DMFDMA affording dihydropyridazine-4carbonitrile 28 that was readily converted into the pyrido[3,4d]pyridazine-4,5-diones 29 on treatment with ammonium acetate and acetic acid. Compound 27 readily reacted with elemental sulphur in the presence of few drops of piperidine yielding arylazoaminothienopyridazine 30 (Scheme 5) (Figure 5) [55]. Typical to the established behaviour of thieno pyridazines compounds, compound **30** reacted with *N*-phenyl maleimide in a mixture of acetic acid and dioxane to yield pyrrolo[3,4-g]phthalazine 33 via intermediary of [4+2] cycloadducts 32. Reaction of compound 30 with DMFDMA afforded the corresponding amidine **34** (Figure 6) [56]. Upon heating compound 34 with ammonium acetate in presence of few drops of acetic acid affords the pyridopyridazine 37 via intermediary of [4+2] cycloadducts 36.

Acylating of compound **30** in acetic acid resulted in the formation of acetylamino **35**. Again up to date no trial to test potential utility of these compounds **27-37** as unique disperse dyes has been made.

5. Synthetic approaches to arylazopyrazoles and pyrazolo pyrimidines

Elnagdi *et al.* have, in the seventies, described efficient syntheses of compounds **38** and **39**.

a 1	D 4	Do	Do	v		M (0.0)	Nº 11(0/)
Compound	R1	R ²	R3	X	Ar	M.p. (°C)	Yield (%)
19a	CH ₃	CH_3	CH_3	Н	-	285	93
19b	C_2H_5	C ₂ H ₅	CH3	Н	-	285	91
19c	C_2H_5	CH_3	CH_3	Н	-	285	91
19d	CH_3	C ₂ H ₅	CH ₃	Н	-	285	91
19e	CH ₃	CH ₃	C_2H_5	Н	-	245	93
19f	C ₂ H ₅	C ₂ H ₅	C_2H_5	Н	-	245	93
19g	C ₂ H ₅	CH ₃	C ₂ H ₅	Н	-	245	94
19h	CH_3	C_2H_5	C_2H_5	Н	-	245	94
19i	-	C ₂ H ₅	C ₆ H ₅ CH ₂	CH ₃	-	229-231	89
19i	-	C ₂ H ₅	C2H5	CH ₃	-	219-220	88
19k	-	C ₂ H ₅	C6H5CH2	Н	-	250-252	90
191	C2H5	C ₂ H ₅	C4H9	н	-	254	90
19m	C ₂ H ₅	C ₂ H ₅	CrH11	Н	-	126	92
19n	C2H5	C ₂ H ₅	C2H7	н	<u> </u>	218-220	82
100	C ₂ H ₅	CoHr	U	и		202	01
190 10n	C ₂ H ₅	CoHr	CHa	и Ц		205	86
10g	C 11	C 11	C II	11		170	00
19q 21a	C2H5	C2H5	C 11	п	-	252 255	90
218			C 11	п		252-255	00
210			C H	Н	-S	215-218	86
21c	-	-	C ₃ H ₇	н	Ĩ,∾ N	210	65
21d	-	-	C ₃ H ₇	Н	HSC-K-N	266-268	80
210		_	C ₂ H ₂ CH ₂	CH ₂	Cette	222-223	92
210 21f			CoHr	CH ₂	C ₆ H ₂ OCH ₂ -n	226-228	92
211 21a			C ₂ H ₅	CH ₂	C ₆ H ₄ OCH ₃ -p	207-209	88
215 21h			C.H-CH-	ц	C.H.	239-240	00
2111			C.H.	и П	C.H.CN o	205	90
211	-	-	C4H9	п		200	(0.02
21]			п	п		200-203	00.05
21K	-	-	H	Н	$C_6H_4SO_3H-p$	198-201	/4.62
211	-		H	H	C ₆ H ₄ OCH ₃ -p	158-161	62.33
21m	-	-	H	Н	C ₆ H ₄ OCH ₃ -p	218-221	64.68
21n	-	-	Н	Н	C ₆ H ₄ CI-p	207-210	/5.5/
210	-	-	CH ₃	Н	C ₆ H ₅	199-201	42.03
21p	-	-	CH ₃	Н	$C_6H_4SO_3H-p$	158-160	90.46
21q	-	-	CH3	Н	C ₆ H ₄ COOH-p	158-160	74.03
21r	-	-	CH ₃	Н	C ₆ H ₄ OCH ₃ -p	143-145	82.54
21s	-	-	CH ₃	Н	C_6H_4Cl-p	172-173	65.05
21t	-	-	CH3	Н	C ₆ H ₄ OH-p	178-180	35.88
22a	-	-	C ₆ H ₅ CH ₂	CH ₃	C ₆ H ₅	280-282	80
22b	-	-	C_2H_5	CH ₃	C ₆ H ₄ OCH ₃ -p	245-246	85
22c	-	-	C_2H_5	CH ₃	C ₆ H ₅	241-243	80
22d	-	-	C6H5CH2	Н	C ₆ H ₅	180-182	78
22e	-	_	C4H9	Н	C ₆ H ₄ CN-0	263	95
24	-	_	-	-	-	262-264	66
						200 201	70



Scheme 4





Figure 5. ORTEP drawing of compound 30.

Compound **38** was patented as dye for keratin fibers and compound **39** was patented by L'Oreal and other companies as constituent of a hair dye formulation. Moreover the biological activity of compound **38** has initially been patented by a Chinese group then published in Journal of Medicinal Chemistry in 2004 [57]. This information prompted us to

continue investigating the potential utility of derivatives of both systems as antimicrobial dyes. Thus compound **42** was synthesized utilizing the approach similar to those utilized by Elnagdi *et al.* [58,59].



Figure 6. ORTEP drawing of compound 34.

Table 5. Yields of compounds 41, 42, 44, 46, 48, 50, 52 and 54.					
Compound	Ar	Ar ¹	Ar ²	M.p. (°C)	Yield (%)
41a	C ₆ H ₅	-	-	134-136	74
41b	C ₆ H ₄ Cl-p	-	-	183-185	81
41c	$C_6H_4NO_2-p$	-	-	140-142	92
41d	C ₆ H ₄ NHCOCH ₃ -p	-	-	215-217	78
42a	C ₆ H ₅	-	-	260-262	54
42b	C ₆ H ₄ Cl-p	-	-	270-270	57
42c	$C_6H_4NO_2-p$	-	-	255-257	60
42d	C ₆ H ₄ OH-p	-	-	245-246	-
42e	C ₆ H ₄ NHCOCH ₃ -p	-	-	268-270	70
44	C ₆ H ₄ OH-p	-	-	287-288	77
46	C ₆ H ₄ OH-p	-	-	248-249	70
48a	C ₆ H ₄ OH-p	C ₆ H ₅	-	301-302	76
48b	C ₆ H ₄ OH-p	$C_6H_4CH_3-p$	-	309-310	84
48c	C ₆ H ₄ OH-p	C ₆ H ₄ Cl-p	-	306-307	78
48d	C ₆ H ₄ OH-p	Fur-2-yl	-	292-293	80
48e	C ₆ H ₄ OH-p	Thien-2-yl	-	276-277	80
50a	C ₆ H ₄ NHCOCH ₃ -p	C ₆ H ₄ Cl-o	-	310-312	75
50b	C ₆ H ₄ NHCOCH ₃ -p	C_6H_4F-p	-	320-322	75
50c	C ₆ H ₄ NHCOCH ₃ -p	C ₆ H ₄ OCH ₃ -p	-	240-242	85
52a	C ₆ H ₄ NHCOCH ₃ -p	C ₆ H ₄ Cl-p	-	330-331	72
52b	C ₆ H ₄ NHCOCH ₃ -p	C_6H_4F-p	-	308-309	73
52c	C ₆ H ₄ NHCOCH ₃ -p	C ₆ H ₄ OCH ₃ -p	-	302-304	79
52d	C ₆ H ₄ NHCOCH ₃ -p	C ₆ H ₃ OCH ₃ -p	-	297-199	74
54a	C ₆ H ₄ NHCOCH ₃ -p	C ₆ H ₅	C ₆ H ₄ OCH ₃ -p	320-322	80
54b	C ₆ H ₄ NHCOCH ₃ -p	C ₆ H ₄ Br-p	C ₆ H ₅	220-222	80
54c	C ₆ H ₄ NHCOCH ₃ -p	C ₆ H ₄ Br-p	C ₆ H ₄ Br-p	308-310	75





Some other researchers [60-63] reported that coupling malononitrile **40** with aryldiazonium chloride afforded arylazomalononitriles, **41**, that subsequently condensed with

hydrazine hydrate to yield 4-arylazo-3,5-diaminopyrazoles, **42**. Al-Etaibi *et al.* [62] has converted compounds **42** into a variety of pyrazolo(1,5-a]pyrimidines **44**, **46** and **48a-e** via condensation with 1,3-diketones 43, enaminonitriles 45, and enaminones 47 (Scheme 6).

Sayed et al. [63] has also converted compounds 42 into pyrazolo(1,5-a]pyrimidines 50a-c, 52a-d and 54a-c, however the structures of the products of addition of ethyl α -cyano cinnamate derivatives 49, arylidenemalononitrile 51 as well as reaction with chalcones 53 need confirmation as it contradicts with all reported data on similar systems. Although it was difficult in the past, now with availability of 2D NMR and ease of producing X-rays such structures can be readily confirmed.

The synthesized dyes 42a,b, 44, 46, 48a-d, 50a-c, 52a-d and 54a-c (Table 5) were applied successfully using high temperature dyeing method and obtained solid shades on polyester fabrics with satisfactory levelness of dyeing and depth of shades, the observed hues ranging from yellow to reddish-violet. The results of fastness properties showed in most cases acceptable to good fastness to light and washing fastness on the polyester fabrics. The antimicrobial activity of dyes 50a-c, 52a-d and 54a-c was also evaluated.

6. Conclusion

We have surveyed recently reported syntheses and dye characteristics of arylazonicotinates, arylazopyridones, arylazo pyridazinone as well as arylazopyrazoles emphasizing their promising potential as disperse dyes for polyester fabrics in the light of successful efforts that made their syntheses both environmentally green and economical methodologies as well as established antimicrobial activities of several newly synthesized dyes.

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