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## Novel styryl and aza-styryl cyanine dyes: Synthesis and spectral sensitization evaluation

Hassan Abazied Shindy\*, Mohamed Abdallah El-Maghraby, Maha Mubark Goma and Nemat Abdelrahman Harb

Department of Chemistry, Faculty of Science, Aswan University, Aswan 81528, Egypt

\*Corresponding author's E. mail: [hashindy2@hotmail.com](mailto:hashindy2@hotmail.com)

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### ABSTRACT

Novel styryl cyanine dyes and aza-styryl cyanine dyes having the nucleus of furo[(3,2-d)pyrazole;(3',2'-d)oxazole] iodide salt were prepared. Spectral sensitization evaluation for all the synthesized styryl and aza-styryl cyanine dyes was carried out through investigating their electronic visible absorption spectra in 95% ethanol solution. The dyes were thought to be better spectral sensitizers when they absorb light at longer wavelength bands (bathochromic shifted and/or red shifted dyes). Consequently the spectral sensitization of the dyes decreased when they absorb light at shorter wavelength bands (hypsochromic shifted and/or blue shifted dyes). The results discussed in this study revealed that the spectral sensitization properties of the examined dyes is highly effected by the type of the X substituted in the phenyl ring system for the styryl cyanine dyes and by the type of the phenyl and/or the naphthyl ring system for the aza-styryl cyanine dyes. Structural confirmations were identified by elemental analysis, visible spectra, IR and  $^1\text{H}$  NMR spectroscopic data.

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**Capsule Summary:** Novel styryl and aza-styryl cyanine dyes were synthesized and the spectral sensitization of as-synthesized dyes has been evaluated.

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### INTRODUCTION

Syryl cyanine dyes (Shindy, 2012; Shindy, 2015; Shindy, 2014) can be used as fluorescence probes in biochemistry and biophysical area (Ephardt and Fromherz, 1989). They are also commonly applied to lasers, electronics and nonlinear optics (Zhao, et al., 1996; Gromov, et al., 1992; He, et al., 1995). Styryl cyanine dyes are a type of important functional cyanine dye, which has been widely applied in many areas, such as frequency-upconverted lasing, optical power limiting, molecular electronics and as novel and

successful fluorescent probes in numerous bioanalytical methods, especially in RNR and DNA analysis (Shindy, 2016; Jedrzejewska, et al., 2003; Hong, et al., 2004; Kovalska, et al., 2005).

In addition, styryl cyanine dyes are also widely used as sensitizers and other additives in the photographic industry (Mees and James, 1979; Hamer, 1964; Pierre, 1984), and these dyes represent an important group of biologically active compounds and are widely applied in the pharmaceutical industry (Preston, 1980).

Besides, styryl cyanine dyes (Antonious, 1997; Kabatc, et al., 2006; Huang and Coull, 2008; Shindy, 2007;

Shim, et al., 2009; Jedrzejewska, et al., 2010; Deligeorgiev, et al., 2010; Vasilev, et al., 2008; Shindy, 2015a; Li, et al., 1998; Matsuoka and Fukunishi, 1996) have a number of good properties, such as ease synthesis, they fluorescent, have higher photostability than the classical cyanine dyes and they can cover the spectrum from the UV to near infrared (NIR) region.

In this research, a novel series of styryl and aza-styryl cyanine dyes as new synthesis contribution were prepared and spectroscopic investigation in the field, and to may be used and/or applied in any of the broad area uses and applications of cyanine dyes, and particularly as photographic sensitizers in photosensitive material industry, as indicators in acid-base titration in analytical chemistry, as probes for determining solvent polarity in solution chemistry and as anti-bacterial strains and anti-fungi strains in pharmaceutical (pharmacological) industry and/or in pharmacology.

## MATERIAL AND METHODS

### General

All the melting points of the prepared compounds are measured using Electrothermal 15V, 45W 1 A9100 melting point apparatus (Chemistry Department, Faculty of Science, Aswan University, Aswan, Egypt) and are uncorrected. Elemental analysis was carried out at the Microanalytical Center of Cairo University by an automatic analyzer (Vario EL III Germany). Infrared spectra were measured with a FT-IR (4100 Jasco, Japan), Cairo University. <sup>1</sup>H-NMR spectra were accomplished using Varian Gemini-300 MHz NMR Spectrometer (Cairo University). Electronic visible absorption spectra were carried out on vis spectrophotometer spectra 24 RS Labomed, INC. (Chemistry Department, Faculty of Science, Aswan University, Aswan, Egypt).

### Synthesis

Synthesis of 4,6-diethyl-5-methyl-7-phenyl-furo[(3,2-d)pyrazolium;(3', 2'-d)oxazolium-3(1)-styryl cyanine dyes (2a-f): 1:1 molar ratios of the quaternized compound (1) (0.01 mol, 0.57 gm) and the aromatic aldehyde (0.01 mol) [benzaldehyde (0.1 gm), 4-hydroxy benzaldehyde (0.12 gm), 4-methoxy benzaldehyde (0.12 gm), p.N-dimethylaminobenzaldehyde (0.15 gm), 4-nitrobenzaldehyde (0.15 gm) or 4-chlorobenzaldehyde (0.14 gm)] were heated under reflux in ethanol (50 ml) as solvent containing piperidine (1 ml) as a catalyst for 6 hrs. The reaction mixture changed from reddish colours to dark brown colours at the end of refluxing. It was filtered while hot to remove any impurities, cooled, and precipitated by ice-water mixture. The styryl cyanine dyes (2a-f) were collected, washed with water several times, dried and crystallized from ethanol, Table (1).

Synthesis of 4,6-diethyl-7-phenyl-furo[(3,2-d) pyrazolium; (3',2'-d)oxazolium-3,5(1)-bis styryl cyanine dyes (3a-f): Two different routes are employed to prepare this series of cyanine dyes:

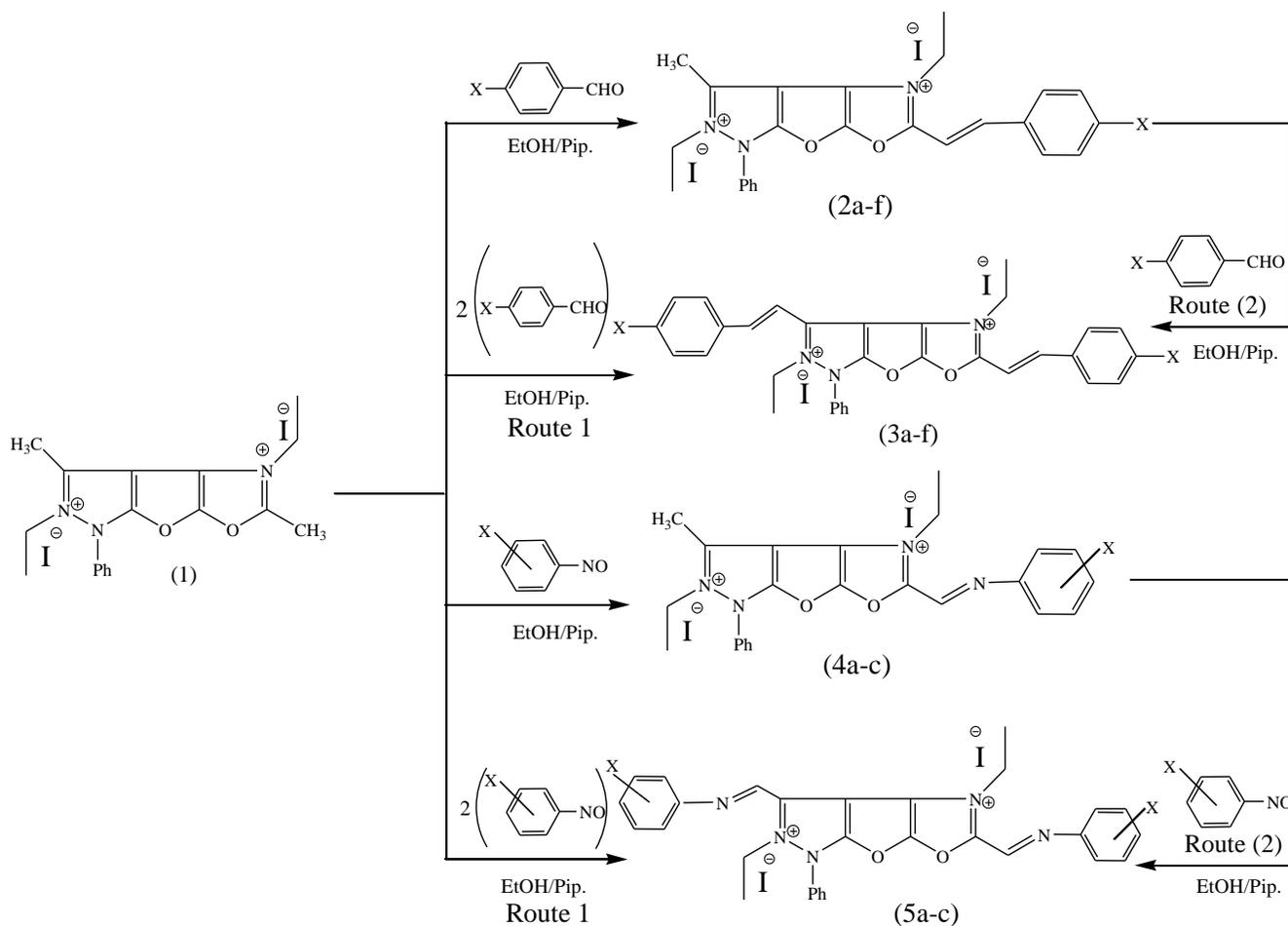
Route (1): unimolar ratios of the quaternized compound (1) (0.01 mol, 0.57 gm) and bimolar ratios of either the aromatic aldehyde (0.02 mol) [benzaldehyde (0.2 gm), 4-hydroxy benzaldehyde (0.24 gm), 4-methoxy benzaldehyde (0.24 gm), p.N-dimethylaminobenzaldehyde (0.3 gm), 4-nitrobenzaldehyde (0.3 gm) or 4-chlorobenzaldehyde (0.28 gm) were heated under reflux in ethanol (50 ml) as solvent containing piperidine (1 ml) as a catalyst for 6 hrs. The reaction mixture changed from reddish color to dark brown at the end of refluxing. It was filtered while hot, cooled, neutralized by glacial acetic acid and precipitated by ice-water mixture. The bis styryl cyanine dyes were collected, washed with water, air dried and crystallized from ethanol, see Table (2).

Route (2): was carried out through dissolving the previously prepared 3(1)-styryl cyanine dyes (2a-f) (0.01 mol) (0.65 gm for 2a, 0.67 gm for 2b, 0.68 gm for 2c, 0.7 gm for 2d, 0.7 gm for 2e, 0.69gm for 2f) and equimolar ratios of either the aromatic aldehyde (0.01 mol) [benzaldehyde (0.1 gm), 4-hydroxy benzaldehyde (0.12 gm), 4-methoxy benzaldehyde (0.12 gm), p.N-dimethylaminobenzaldehyde (0.15 gm), 4-nitrobenzaldehyde (0.15 gm) or 4-chlorobenzaldehyde (0.14 gm)] in ethanol (50 ml), containing piperidine (1 ml). The reacting materials were heated under reflux for 6 hours, and attained a permanent intense brown colour at the end of the reflux. It was filtered off while hot, concentrated, cooled, neutralized by acetic acid and precipitated by adding cold water. The precipitates were collected and recrystallized from ethanol to give the same 3,5(1)-bis styryl cyanine dyes obtained by route (1), characterized by melting points, mixed melting points, same visible IR and <sup>1</sup>H-NMR spectral data.

Synthesis of 4,6-diethyl-5-methyl-7-phenylfuro[(3,2-d)pyrazolium;(3', 2'-d)oxazolium-3[2(1)]-aza-styryl cyanine dyes (4a-c): An equimolar ratios of the quaternized compound (1) (0.01 mol, 0.57 gm) and nitroso compounds (0.01 mol) of either 4-nitroso phenol (0.12 gm), 1-nitroso-2-naphthol (0.17 gm) or 2-nitroso-1-naphthol (0.17 gm) in ethanol (50 ml) containing piperidine (1 ml) were heated under reflux for 6 hrs. The reaction mixture which attained a deep permanent colour at the end of the refluxing time was filtered on hot to remove any impurities, precipitated using ice-water mixture, filtered and air dried. The aza-styryl cyanine dyes (4a-c) were collected and crystallized using ethanol. See the data given in Table (3).

Synthesis of 4,6-diethyl-7-phenyl-furo[(3,2-d) pyrazolium; (3',2'-d)oxazolium-3,5[2(1)]-bis aza-styryl cyanine dyes (5a-c): This synthesis was proceeded through two different routes as following:

Route (1): Amixture of unimolar ratios of the quaternized compound (1) (0.01 mol, 0.57 gm) and bimolar ratios of the nitroso compounds (0.02 mol) of either [4-



**Scheme 1:** Synthesis Strategy of the prepared compounds (2a-f), (3a-f), (4a-c), and (5a-c)

[(2a-f), (3a-f): X = H (a), OH (b), OCH<sub>3</sub> (c), (CH<sub>3</sub>)<sub>2</sub>N (d), NO<sub>2</sub> (e), Cl (f), (4a-c), (5a-c): X = 4-OH (a), 2,0H, 3, 4-benzo (b), 2,0H, 5, 6-benzo (c)].

nitroso phenol (0.24 gm), 2-nitroso-1-naphthol (0.34 gm), or 1-nitroso-2-naphthol (0.34 gm)] in ethanol (50 ml) containing basic catalyst piperidine (1 ml) were heated under reflux for 6 hrs. The reaction mixture was filtered on hot to remove impurities, precipitated using crushed ice, neutralized with glacial acetic acid, collected and crystallized using ethanol. See Table (3).

Route (2): Was carried out through dissolving the previously prepared aza-styryl cyanine dyes (4a-c) (0.01 mol, 0.67 gm for 4a, 0.72 gm for 4b, 0.72 gm for 4c) and equimolar ratios of the nitroso compounds (0.01 mol) of either [4-nitroso phenol (0.24 gm), 2-nitroso-1-naphthol (0.34 gm), or 1-nitroso-2-naphthol (0.34 gm)] in ethanol (50 ml) containing piperidine (1 ml). The reacting materials were heated under reflux for 6 hrs and attained a permanent intense brown colour at the end of the reflux. It was filtered off while hot, concentrated, cooled, neutralized by acetic acid and precipitated by adding cold water. The precipitates were collected and recrystallized from ethanol to give the same bis aza-styryl cyanine dyes (5a-c) obtained by route (1), Table

(3), characterized by melting points, mixed melting points, same visible, IR and <sup>1</sup>H-NMR spectral data.

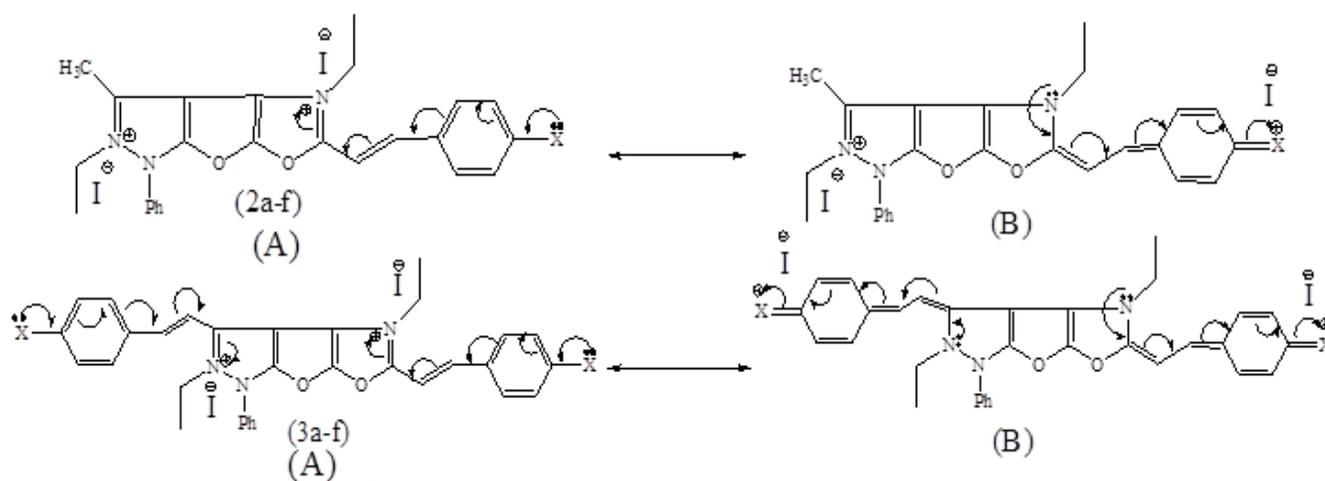
### Spectral studies

The electronic visible absorption spectra of the prepared cyanine dyes were examined in 95% ethanol solution and recorded using 1Cm Qz cell in visible spectrophotometer, spectro 24 RS Labomed, INC. A stock solution (1x10<sup>-3</sup>M) of the dyes was prepared and diluted to a suitable volume in order to obtain the desired lower concentrations. The spectra were recorded immediately to eliminate as much as possible the effect of time.

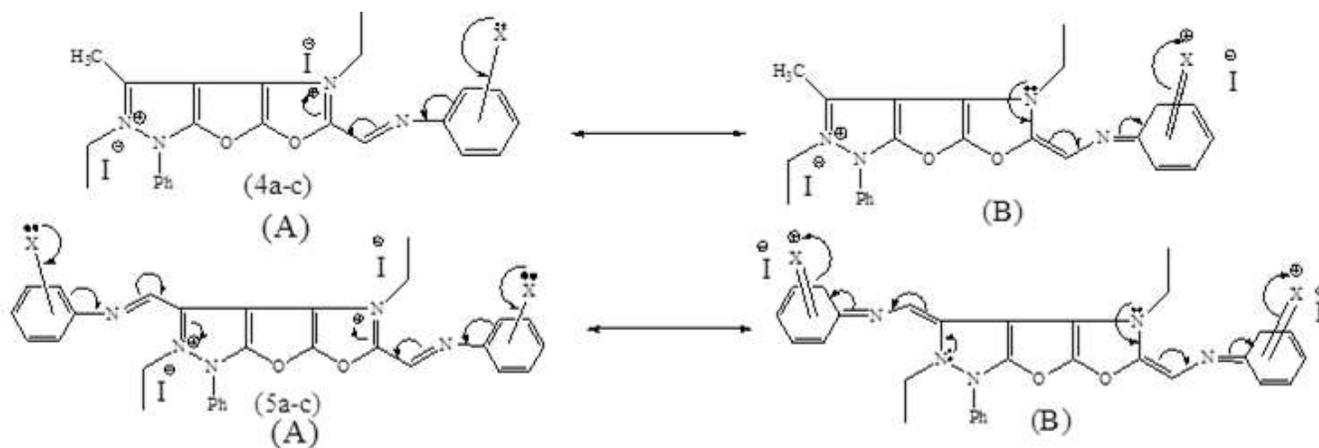
## RESULTS AND DISCUSSION

### Synthesis

Reaction of the compound 4,6-diethyl-3,5-dimethyl-7-phenyl-furo[(3,2-d) pyrazolium;(3',2'-d)oxazolium]



**Scheme 2a:** Colour intensity and the electronic charge transfer pathways illustration of the synthesized styryl cyanine (bis styryl cyanine) dyes 2a-f (3a-f).



**Scheme 2b:** Colour intensity and the electronic charge transfer pathways illustration of the synthesized aza-styryl cyanine (bis aza-styryl cyanine) dyes 2a-f (3a-f).

diiodide quaternary salt (1) and an equimolar or bimolar ratios of the given aromatic aldehydes, (benzaldehyde, p.OH benzaldehyde, p.OCH<sub>3</sub> benzaldehyde, p.N(CH<sub>3</sub>)<sub>2</sub> benzaldehyde, p.NO<sub>2</sub> benzaldehyde, p.Cl benzaldehyde) in ethanol containing piperidine as a basic catalyst afforded the 3(1)-styryl cyanines (2a-f) or 3,5(1)-bis styryl cyanines (3a-f) (Scheme 1, Route 1).

Chemical confirmations for the 3,5(1)-bis styryl cyanine dyes (3a-f) were also carried out through Route (2), Scheme (1) via reactions of the previously prepared 3(1)-styryl cyanine dyes (2a-f) with an equimolar ratios of the aromatic aldehydes (benzaldehyde, 4-hydroxy benzaldehyde, 4-methoxy benzaldehyde, p.N-dimethylaminobenzaldehyde, 4-nitrobenzaldehyde and 4-chlorobenzaldehyde) in ethanol containing piperidine to achieve the same 3,5(1)-bis styryl cyanine dyes (3a-f) obtained through Route (1), characterized by the same melting points, mixed melting points, the same visible, IR and <sup>1</sup>H-NMR spectra (Scheme 1, Route 2).

The reaction of the diquaternized compound (1) with equimolar and/or bimolar ratios of nitroso compounds (4-nitroso phenol, 2-nitroso-1-naphthol, or 1-nitroso-2-naphthol) in ethanol containing basic catalyst piperidine yielded the aza-styryl cyanine dyes (4a-c) and/or the bis aza-styryl cyanine dyes (5a-c), respectively (Scheme 1, Route 1).

Chemical confirmations were carried out through the reactions of the previously prepared aza-styryl cyanine dyes (4a-c) with equimolar ratios of the nitroso compounds (4-nitroso phenol, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol) in ethanol catalyzed by piperidine through Route (2), to achieve the same bis aza-styryl cyanine dyes (5a-c) obtained by Route (1), characterized by the same melting points, mixed melting points, the same visible, IR and <sup>1</sup>H-NMR spectra (Scheme 1, Route 2).

The structure of the prepared compound was characterized and identified by elemental analysis, Tables (1), (2) and (3),

**Table 1:** Characterization of the prepared compounds (2a-f)

Coms	Colour	Yield %	M. P °C	MF (MW)	Composition analysis (%)						Abs. (in 95% ethanol)	
					Calculated			Found			$\lambda_{\max}$	$\epsilon_{\max}$
					C	H	N	C	H	N	nm	mol <sup>-1</sup> .cm <sup>2</sup>
2a	Deep brown	42	140	C <sub>25</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub> I <sub>2</sub> (653)	45.94	8.83	6.43	45.92	8.79	6.41	440, 460, 600	13240, 13370, 6800
2b	Deep brown	53	125	C <sub>25</sub> H <sub>25</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> (669)	44.84	3.74	6.28	44.81	3.69	6.22	450, 470, 610	12050, 11680, 6600
2c	Deep brown	43	150	C <sub>26</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> I <sub>2</sub> (683)	45.68	3.95	6.15	45.63	3.93	6.12	480, 520, 620	11370, 10150, 6120
2d	Deep brown	45	115	C <sub>27</sub> H <sub>30</sub> N <sub>4</sub> O <sub>2</sub> I <sub>2</sub> (696)	46.55	4.31	8.05	46.51	4.28	8.01	480, 500, 530, 630	12600, 14110, 12400, 6150
2e	Deep brown	48	145	C <sub>25</sub> H <sub>24</sub> N <sub>4</sub> O <sub>4</sub> I <sub>2</sub> (698)	42.98	3.44	8.02	42.95	3.41	8.01	430, 450, 490, 590	9690, 11020, 10530, 4990
2f	Deep brown	50	130	C <sub>25</sub> H <sub>24</sub> N <sub>3</sub> O <sub>2</sub> I <sub>2</sub> Cl (687.6)	43.63	3.49	6.11	43.59	3.44	6.8	420, 450, 580	13770, 13850, 7410

Coms = Compounds, MF = Molecular formula, MW = Molecular weight and Abs = absorbance

**Table 2:** Characterization of the prepared compounds (3a-f)

Coms	Colour	Yield %	M. P °C	MF (MW)	Composition analysis (%)						Abs. (in 95% ethanol)	
					Calculated			Found			$\lambda_{\max}$	$\epsilon_{\max}$
					C	H	N	C	H	N	nm	mol <sup>-1</sup> .cm <sup>2</sup>
3a	Deep brown	49	145	C <sub>32</sub> H <sub>29</sub> N <sub>3</sub> O <sub>2</sub> I <sub>2</sub> (741)	51.82	3.91	5.67	51.8	3.89	5.64	460, 480, 610	12570, 14100, 7490
3b	Deep brown	52	135	C <sub>32</sub> H <sub>29</sub> N <sub>3</sub> O <sub>4</sub> I <sub>2</sub> (773)	49.68	3.75	5.43	49.65	3.71	5.41	460, 490, 620	11760, 13570, 6370
3c	Deep brown	57	160	C <sub>34</sub> H <sub>33</sub> N <sub>3</sub> O <sub>4</sub> I <sub>2</sub> (801)	50.94	4.12	5.24	50.91	4.09	5.21	470, 500, 630	12280, 13110, 6320
3d	Deep brown	46	120	C <sub>36</sub> H <sub>39</sub> N <sub>5</sub> O <sub>2</sub> I <sub>2</sub> (827)	52.24	4.72	8.46	52.22	4.68	8.41	480, 500, 540, 640	13160, 15210, 12870, 6330
3e	Deep brown	49	150	C <sub>32</sub> H <sub>27</sub> N <sub>5</sub> O <sub>6</sub> I <sub>2</sub> (831)	46.21	3.25	8.42	46.17	3.22	8.4	450, 470, 500, 600	8520, 10640, 8000, 4490
3f	Deep brown	54	135	C <sub>32</sub> H <sub>27</sub> N <sub>3</sub> O <sub>2</sub> I <sub>2</sub> Cl <sub>2</sub> (810)	47.41	3.33	5.19	47.39	3.28	5.15	440, 460, 590	10670, 11760, 6870

Explanations as in Table 1

visible spectra, Tables (1), (2) and (3), IR (Wade, 1999) and <sup>1</sup>H-NMR (Wade, 1999a) spectroscopic data, Table (4).

### Spectral sensitization evaluation

Spectral sensitization evaluation for all the synthesized cyanine dyes was carried out through investigating their electronic visible absorption spectra in 95% ethanol solution. The dyes were thought to be better spectral sensitizers when they absorb light at longer wavelength bands (bathochromic shifted and/or red shifted dyes).

Consequently the spectral sensitization of the dyes decrease when they absorb light at shorter wavelength bands (hypsochromic shifted and/or blue shifted dyes). So, we may say that the spectral sensitization of one dye is higher than the other one if the wavelength of the maximum absorption spectrum of the former one is longer than that of the latter one. Inversely, we may say that the spectral sensitization of one dye is lower than the other one if the wavelength of the maximum absorption spectrum of the former one is shorter than that of the latter one (Shindy, et al., 2017; Shindy, 2017).

**Table 3:** Characterization of the prepared compounds (4a-c) and (5a-c)

Coms	Colour	Yield %	M. P °C	MF (MW)	Composition analysis (%)						Abs. (in 95% ethanol)	
					Calculated			Found			$\lambda_{\max}$ nm	$\epsilon_{\max}$ mol <sup>-1</sup> .cm <sup>2</sup>
					C	H	N	C	H	N		
4a	Deep brown	55	120	C <sub>24</sub> H <sub>24</sub> N <sub>4</sub> O <sub>3</sub> I <sub>2</sub> (670)	42.99	3.58	8.36	42.95	3.54	8.33	440, 580	14220, 7030
4b	Deep brown	58	135	C <sub>28</sub> H <sub>26</sub> N <sub>4</sub> O <sub>3</sub> I <sub>2</sub> (720)	46.67	3.61	7.78	46.64	3.59	7.74	460, 590	12680, 9940
4c	Deep brown	56	160	C <sub>28</sub> H <sub>26</sub> N <sub>4</sub> O <sub>3</sub> I <sub>2</sub> (720)	46.67	3.61	7.78	46.62	3.57	7.73	470, 600	12210, 8370
5a	Deep brown	59	130	C <sub>30</sub> H <sub>27</sub> N <sub>5</sub> O <sub>4</sub> I <sub>2</sub> (775)	46.45	3.48	9.03	46.43	3.45	9.01	450, 590	15480, 7970
5b	Deep brown	60	145	C <sub>38</sub> H <sub>31</sub> N <sub>5</sub> O <sub>4</sub> I <sub>2</sub> (875)	52.11	3.54	8	52.09	3.51	7.97	460, 600	11990, 8440
5c	Deep brown	62	170	C <sub>38</sub> H <sub>31</sub> N <sub>5</sub> O <sub>4</sub> I <sub>2</sub> (875)	52.11	3.54	8	52.08	3.52	7.98	480, 510, 610	12780, 11700, 7380

Explanations as in Table 1

Spectral sensitization evaluation study is very important in the case of cyanine dyes because the extensive uses of these dyes in photographic material industry to increase the sensitivity range of silver halide emulsion by making an increase in the range of wavelength which form an image on the film.

The visible electronic absorption spectra of the styryl cyanine dyes (bis styryl cyanine dyes) 2a-f (3a-f) in 95% ethanol solution gives bands in visible region 440-630 nm (460-640 nm). These bands underwent displacements to give bathochromic shifts (red shifts) and or hypsochromic shifts (blue shifts) in addition to increasing and or decreasing the intensity of the absorption bands depending upon the type of the X substituents in the phenyl ring system, Tables (1) and (2).

So, substituting X = H in dyes 2a (3a) by X = OH, OCH<sub>3</sub> and or N(CH<sub>3</sub>)<sub>2</sub> to obtain dyes 2b (3b), 2c (3c) and or 2d (3d) makes bathochromic shifts for the absorption bands by 10 nm, 20 nm, 30 nm, in addition to increasing for the intensity of the bands, respectively, Tables (1) and (2). This can be attributed to the electron pushing characters of the OH, OCH<sub>3</sub> and or N(CH<sub>3</sub>)<sub>2</sub> groups in the latter dyes, which increase and or facilitate the intensity of the electronic charge transfer to the quaternary nitrogen atom of the pyrazolium and or oxazolium iodide salt (acidic center of the dyes) and consequently red shifts occurs for the bands of these latter dyes 2b (3b), 2c (3c), 2d (3d) in correspondence to the former parent dyes 2a (3a).

Substituting X = H by X = NO<sub>2</sub> and or Cl moving from dyes 2a (3a) to 2e (3e) and or 2f (3f) causes blue shifts for the absorption bands by 10 nm and or 20 nm, accompanied by quenching the intensity of these bands, respectively, Tables (1) and (2). This can be related to the strong electron pulling characters of the NO<sub>2</sub> group and or the Cl atom in the latter dyes 2e (3e) and or 2f (3f) which

make decreasing for intensity of electronic charge transfer to the quaternary nitrogen of pyrazolium and or oxazolium salt residue (acidic center of the dyes), and accordingly hypsochromic shifts occurs in the spectra of the latter dyes 2e (3e) and or 2f (3f) in correspondence to the parent dyes 2a (3a).

Comparing the electronic visible absorption spectra of the styryl cyanine dyes (2a-f) with those of the bis styryl cyanine dyes (3a-f) declared that the latter dyes have bathochromically shifted bands related to the former ones, Tables (1) and (2). This can be attributed to the presence of two factors. The first factor is the presence of two electronic charge transfer pathways inside the latter dyes molecules in correspondance to one electronic charge transfer pathways inside the former dyes molecules, Scheme (2a). The second factor is increasing conjugation due to increasing the number of methine units (=CH-) in bis styryl cyanine dyes (3a-f) related to the former styryl cyanine dyes (2a-f) by two methine units (Scheme 1).

Additionally, the visible electronic transitions absorption spectra of the aza-styryl cyanine dyes (bis aza-styryl cyanine dyes) 4a-c (5a-c) in 95% ethanol solution reveals bands in the visible region 440-600 nm (450-610 nm). The positions of these bands and their molar extinction coefficients are largely effected by the type of the phenyl and or the naphthyl ring system in the dyes molecules and by the higher and or lower planarity of the dyes, Table (3).

So, substituting the benzene ring system in dyes 4a (5a) by naphthyl ring system to give dyes 4b (5b) and or 4c (5c) resulted in a noticeable bathochromic shifts for the absorption bands by 10 nm and or 20 nm in addition to increasing the intensity of the bands, respectively, Table (3). This can be attributed to increasing  $\pi$ -delocalization conjugation the latter dyes 4b (5b), 4c (5c) due to the

**Table 4:** IR and <sup>1</sup>H NMR spectral data of the prepared compounds (2a), (3a), (4a) and (5a)

Compound	IR Spectrum (KBr, Cm <sup>-1</sup> ).	<sup>1</sup> H NMR Spectrum (DMSO, δ).
2a	604, 689, 755 (monosubstituted phenyl).	1.2-1.9 (m, 6H, 2CH <sub>3</sub> of positions 5, 6).
	1155 (C—O—C cyclic).	2-2.4 (m, 2H, CH <sub>2</sub> of position 6).
	1308, 1364 (C—N).	3-3.2 (m, 3H, CH <sub>3</sub> of position 4).
	1493 (C=N).	3.3-3.8 (m, 2H, CH <sub>2</sub> of position 4).
	1602 (C=C).	4.5-4.7 (m, 2H, 2 —CH=).
	2925, 2860 (quaternary salt).	6.7-8.3 (m, 10H, aromatic).
3a	605, 691, 754 (monosubstituted phenyl).	1.1-1.9 (m, 3H, CH <sub>3</sub> of position 6).
	1065, 1157 (C—O—C cyclic).	2-2.4 (m, 2H, CH <sub>2</sub> of position 6).
	1366, 1308 (C—N).	3-3.2 (m, 3H, CH <sub>3</sub> of position 4).
	1492 (C=N).	3.3-3.8 (m, 2H, CH <sub>2</sub> of position 4).
	1598 (C=C).	4.6 (m, 4H, 4 —CH=).
	2929, 2856 (quaternary salt).	6.6-8.2 (m, 15H, aromatic).
4a	690, 756 (monosubstituted phenyl).	1-1.8 (m, 6H, 2CH <sub>3</sub> of positions 5, 6).
	829, 903 (p.disubstituted phenyl).	1.9-2.4 (m, 2H, CH <sub>2</sub> of position 6).
	1027, 1122 (C—O—C cyclic).	2.7-3 (m, 3H, CH <sub>3</sub> of position 4).
	1363 (C—N).	3.2-3.7 (m, 2H, CH <sub>2</sub> of position 4).
	1496, 1442 (C=N).	4.5-4.7 (m, 1H, —CH=).
	1602 (C=C).	6.7-8.4 (m, 10H, aromatic + 1 OH).
	2929(quaternary salt).	
3062 (phenolic OH).		
5a	646, 690 (monosubstituted phenyl).	1-1.9 (m, 3H, CH <sub>3</sub> of position 6).
	756, 828 (p.disubstituted phenyl).	2-2.4 (m, 2H, CH <sub>2</sub> of position 6).
	1023, 1130 (C—O—C cyclic).	2.7-3.1 (m, 3H, CH <sub>3</sub> of position 4).
	1362 (C—N).	3.2-3.8 (m, 2H, CH <sub>2</sub> of position 4).
	1496 (C=N).	4.6 (m, 2H, 2 —CH=).
	1599 (C=C).	6.6-8.5 (m, 15H, aromatic + 2 OH).
	2930 (quaternary salt).	
3058 (phenolic OH).		

presence of naphthyl ring systems in correspondence to phenyl ring system in the former dyes 4a (5a).

It also, interested to notice that, substituted X = 2.OH, 5, 6-benz by X = 2.OH, 3, 4-benz transferring from dyes 4b (5b) to dyes 4c (5c) cause bathochromic shifts for the absorption bands by 10 nm, Table (3). This may be related to the higher structure planarity of the dyes 4c (5c) in correspondence to the lower structure planarity of the dyes 4b (5b). Higher structure planarity dyes make easier, faster and facilitate the electronic charge transfer pathways to the quaternary pyrazolium and or oxazolium salt residue, and consequently, bathochromic shifts occurs. Inversely, lower structure planarity dyes resulted in difficulty and slowing the electronic charge transfer pathways to the quaternary pyrazolium and or oxazolium salt residue, and accordingly hypsochromic shifts occurs.

Comparing the electronic visible absorption spectra of the aza-styryl cyanine dyes (4a-c) with those of the bis aza-styryl cyanine dyes (5a-c) declared that the latter dyes have bathochromically shifted bands related to the former ones, Table (3). This can be attributed to the presence of two factors. The first factor is the presence of two electronic charge transfer pathways inside the latter dyes molecules in correspondance to one electronic charge transfer pathways inside the former dyes molecules, Scheme (2b). The second factor is increasing conjugation due to increasing the number of aza-methine units (-CH=N-) in bis aza-styryl cyanine dyes (5a-c) related to the former aza-styryl cyanine dyes (4a-c) by one aza-methine unit (Scheme 1).

## CONCLUSIONS

The electronic visible absorption spectra of styryl cyanine dyes (bis styryl cyanine dyes) 2a-f (3a-f) and or the aza-styryl cyanine dyes (bis aza-styryl cyanine dyes) 4a-c (5a-c) in 95% ethanol solution underwent displacements to give bathochromic and or hypsochromic band shifts in addition to increasing and or decreasing the intensity of the absorption bands depending upon various factors. Presence of either electron releasing and or attracting groups in the dyes molecules in the order of: electron pushing group dyes > electron pulling group dyes (for the styryl and bis styryl cyanine dyes). Presence of phenyl and or naphthyl ring system in the order of: naphthyl dyes > phenyl dyes (for aza-styryl, bis aza-styryl cyanine dyes). Planarity of the dyes structures in the order of: higher planarity dyes > lower planarity dyes (for the aza-styryl and bis aza-styryl cyanine dyes). Increasing and or decreasing the number of the electronic charge transfer pathways inside the dyes molecules in the order of: two electronic charge transfer pathways dyes > one electronic charge transfer pathways dyes (for the styryl cyanine dyes, bis styryl cyanine dyes, aza-styryl cyanine dyes and bis aza-styryl cyanine dyes). Increasing and or decreasing conjugation due to increasing and or decreasing the number of the methine units inside the dyes structure, in the order of: more methine units dyes > less methine units dyes (for the styryl cyanine dyes, bis styryl cyanine dyes). Increasing and or decreasing conjugation due to increasing and or decreasing the the number of the aza-methine units inside the dyes structure, in the order of: more aza-methine units dyes > less aza-methine units dyes (for the aza-styryl cyanine dyes and bis aza-styryl cyanine dyes).

The intensity of the colour of the styryl cyanine dyes (bis styryl cyanine dyes) 2a-f (3a-f) and or the aza-styryl cyanine dyes (bis aza-styryl cyanine dyes) 4a-c (5a-c) can be related to suggested two mesomeric electronic transitions structures (A) and (B) producing a delocalized positive charge over the conjugated chromophoric group system of the dyes, Scheme (2a, b).

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