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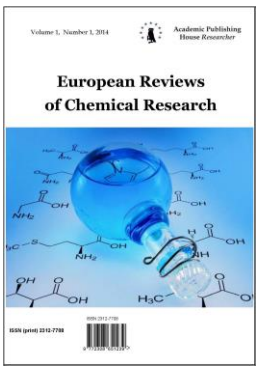

Synthesis and Visible Spectra Studies of Novel Pyrazolo/Oxazole Merocyanine Dyes

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Abstract

Novel acyclic merocyanine dyes and cyclic merocyanine dyes derived from the nucleus of furo[(3,2-d)pyrazole;(3',2'-d)oxazole] were prepared. The electronic visible absorption spectra of all the new synthesized acyclic and cyclic merocyanine dyes were examined in 95 % ethanol solution to evaluate their spectral sensitization properties. Studying the electronic visible absorption spectra of cyanine dyes in 95 % ethanol solution have a great practical value and is very important study in the case of cyanine dyes because the extensive uses and applications of these dyes as photographic sensitizers for silver halide emulsion in photosensitive material industry for coloured and non coloured (black and white) films (cyanine dyes were originally used, and still are, to increase the sensitivity range of photographic emulsions, i.e. to increase the range of wavelengths which will form an image on the film). Structural characterization and identification was carried out via elemental analysis, visible spectra, mass, IR and ^{1}H NMR spectroscopic data.

Keywords: cyanine dyes, merocyanine dyes, synthesis, visible absorption spectra, acyclic merocyanine, cyclic merocyanine.

1. Introduction

Merocyanine dyes (Shindy et al., 2012; Shindy et al., 2016; Shindy et al., 2008) have found wide application in various areas of science and technology. They are used as optical sensors, spectral sensitizers for silver halide photography (Peng et al., 1996; Chen et al., 1995; Araki et al., 1997), and recording medium in optical disks. Their potential application as photosensitizers for photodynamic therapy (PDT) (Gomer et al., 1991; Krieg et al., 1993; Redmond et al., 1994) and radiation sensitizers for solid tumor treatment (Harriman et al., 1991) has been extensively studied. Merocyanine dyes are promising materials for future technological applications, including nonlinear optics, solar and hydrogen energy, laser technology, and nanotechnology.

In addition, it is worthy of special attention that merocyanines (often called photomerocyanines) are obtained during the UV irradiation or heating of spiropyrans (Bertelson, 1999; Minkin, 2004; Lukyanov, Lukyanova, 2005). Their photo- and thermochromic properties are of considerable interest, and spiropyrans have been proposed for optical memory and switches (Berkovic, et al., 2000), metal ions extraction (Alfimov et al., 2003; Kimura et al., 2004), photocontrollable ferromagnetics (Taguchi et al., 2003; Kashima et al., 2005), and optical and fluorescence sensors on metal ions and biological objects (Evans et al., 1993; Voloshin et al., 2004; Tomizaki et al., 2005).

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Besides, merocyanine dyes are heterocyclic chromophores that are extensively used in a number of areas (i.e., as photographic sensitizers, for nonlinear optics, and in chemotherapy) (Chen et al., 2006; Yow et al., 2000; Zareba et al., 2005; Marder, 2006; Marder et al., 1993; Brooker et al., 1951). Recently they have also been employed as sensors of protein conformation and protein interactions in live cell imaging (Nalbant et al., 2004). The efficacy of merocyanine dyes as components of biosensors depends not only on their fluorescence emission properties, but also not their photostability.

In this research paper we prepared novel series of acyclic and cyclic merocyanine dyes as new synthesis contribution and spectroscopic investigation in the field, and to may be used and/or applied in any of the wide uses and applications of cyanine dyes, and particularly as photographic sensitizers in photographic material industry, as indicators in operations of acid-base titration in analytical chemistry, as probes for determining solvent polarity in physical, physical organic and/or in inorganic chemistry and as bactericidal and fungicidal in pharmaceutical (pharmacological) industry and/or in pharmacochemistry.

2. Results and discussion

2.1. Synthesis

Oxidation of the compound 3,5-dimethyl-7-phenyl-furo[(3,2-d)pyraz ole;(3',2'-d) oxazole] (1) with bimolar ratios of selenium dioxide, yielded the compound 3,5-dicarbaldehyde-7-phenyl-furo[(3,2-d)pyrazole;(3',2'-d)oxazole] (2), Scheme (1).

Subsequent reaction of the diformyl compound (2) with equimolar or bimolar ratios of acyl and/or acyl derivatives (acetaldehyde, acetone, acetophenone, p-methoxyacetophenone, or p-nitroacetophenone) in ethanol as organic solvent containing piperidine as a basic catalyst resulted the acyclic merocyanine dyes (3a-e) or bis acyclic merocyanines (4a-e). See Scheme (1), Route (1).

Chemical confirmations for the bis acyclic merocyanine dyes (4a-e) were carried out through, Route (2), via reactions of the previously prepared acyclic merocyanine dyes (3a-e) with equimolr ratios of the acyl and/or acyl derivatives (acetaldehyde, acetone, acetophenone, p-methoxyacetophenone, p-nitroacetophen-one) in ethanol containing few drops of piperidine to achieve the same bis acyclic merocyanine dyes (4a-e) obtained through Route 1, characterized by the same melting points, mixed melting points, the same visible, IR and ^{1}H-NMR spectra. Scheme (1).

In addition, the diformyl compound (2) was reacted with equimolar or bimolar ratios of acetylacetone or ethylacetoacetate in ethanol as solvent containing piperidine as basic catalyst and resulted the acyclic merocyanine dyes (5a, b) or bis acyclic mero cyanines (6a, b). See Scheme (1), Route (1).

Chemical confirmations for the bis acyclic merocyanine dyes (6a, b) were carried out through, Route (2), via reactions of the previously prepared acyclic merocyanine dyes (5a, b) with equimolr ratios of acetylacetone or ethylacetoacetate in ethanol and presence of piperidine to achieve the same bis acyclic merocyanine dyes (6a, b) obtained through Route (1), characterized by the same melting points, mixed melting points, the same visible, IR and ^{1}H-NMR spectra, Scheme (1).

Besides, an equimolar and/or bimolar ratios of hydantoin (imidazolid-2, 4-dione) were reacted with the diformyl compound (2) in ethanol as organic solvent containing piperidine as a basic catalyst and achieved cyclic merocyanine or bis cyclic merocyanine dyes (7) and (8) respectively, Scheme (1).

Chemical confirmations were carried out through the reaction of the previously prepared cyclic merocyanine dye (7) and equimolar ratios of hydantoin in ethanol and presence of piperidine through Route (2), to achieve the same bis cyclic merocyanine dye (8) obtained through Route (1), characterized by the same melting points, mixed melting points, the same visible, IR and ^{1}H-NMR spectra, Scheme (1).

The structures of the prepared compounds was characterized and identified by elemental analysis,Tables (1), (2) and (3) visible spectra, Tables 1, 2 and 3, Mass spectrometer, IR (Wade, 1999) and ^{1}H NMR (Wade, 1999a) spectroscopy, Table 4.

2.2. Visible spectra studies

The electronic visible absorption spectra of the acyclic merocyanine dyes (3a-e) and the bis acyclic merocyanine dyes (4a-e) in 95 % ethanol solution reveal bands in the visible region 440-620 nm and 390-630 nm, respectively. The positions of these bands underwent displacements to give

bathochromic shifts and/or hupsochromic shifts accompanied by increasing and / or decreasing the intensity of the bands depending upon the type of the side chain substituent (R), Tables (1) and (2).

So, substituting R = H in the acyclic (bis acyclic) merocyanine dyes 3a (4a) by R = CH_3 to give dyes 3b (4b) caused bathochromic shifts for the absorption band by 10 nm in addition to increasing the intensity of the bands, Tables (1) and (2). This can be attributed to the electron donating character of the CH_3 group in the latter dyes 3b (4b) which facilitate and increases the strength and intensity of the electronic charge transfer to the positive center of the carbonyl group and consequently red shifts occurs in correspondence to the H atom in the former dyes 3a (4a).

In addition, substituting R = H by R = ph moving from dyes 3a (4a) to dyes 3c (4c) resulted in a red shifts by 20 nm accompanied with increasing the intensity of the absorption bands, Tables 1 and 2. This can be related to increasing π-delocalization conjugation in the latter dyes 3c (4c) due to the presence of additionally phenyl ring system.

Besides, substituting R = ph in the dyes 3c (4c) by R = C_6H_5-p.OCH_3 and / or C_6H_4-p.NO_2 to give dyes 3d (4d) and / or 3e (4e) makes bathochromic and / or hypsochromic shifts for the absorption bands by 10 nm and / or 30 nm, accompanied by quenching the intensity of the bands, respectively, Tables (1) and (2). This can be related to the electron releasing character of the methoxy group in dyes 3d (4d) and / or the electron attracting character of the NO_2 group in the dyes 3e (4e). Electron releasing groups increase the strength of the intensity of electronic charge transfer from the basic center of the dye (oxygen atom and / or nitrogen atom) to the acidic center of the dye (polarized carbonyl group) and consequently red shifts occurs. Electron attracting groups decreases the strength of the intensity of electronic charge transfer pathways from the basic center of the dye (oxygen atom and/or nitrogen atom) to the polarized acidic center of the dye (carbonyl group), and accordingly blue shift occurs, Scheme (2).

Comparing the electronic visible absorption spectra of the acyclic merocyanine dyes (3a-e) with those of the bis acyclic merocyanine dyes (4a-e) 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 (2). The second factor is increasing conjugation due to increasing the number of methine units in bis acyclic merocyanine dyes (4a-e) related to the former acyclic merocyanine dyes (3a-e) by two methine unit. Scheme (1).

Additionally, the electronic visible absorption spectra of the acyclic (bis acyclic) merocyanine dyes 5a, b (6a, b) and cyclic (bis cyclic) merocyanine dyes 7 (8) disclose bands in the visible region 420-590 nm (440-600 nm) and 600-610 nm respectively. The positions of these bands and their molar extinction coefficients are influenced by the kind of R substituted in the dyes 5a, b (6a, b) molecules and by the cyclic ring system in dyes 7 (8), Table (3). So, substituting R = COOEt by R = $COCH_3$ transferring from dyes 5a (6a) to dyes 5b (6b) makes a remarkable bathochromic shifts for the absorption bands by 10 nm. This can be related to the strong powerful electron pulling character of the ethoxy group in the former dyes 5a (6a) in correspondence to the strong electron pushing character of the methyl group in the latter dyes 5b (6b).

Furthermore, comparing the electronic visible absorption spectra of the acyclic merocyanine dyes 5a, b (6a, b) with those of the cyclic merocyanine dyes 7 (8) showed that the latter cyclic merocyanine dyes 7 (8) reveals bathochromic shifted band by 10 nm and 20 nm in addition to increasing the intensity of the bands, Table 3. This may be attributed to the presence of two basic center (two nitrogen atoms) in the cyclic ring system of the latter dyes 7 (8), which facilitate and increase the intensity of electronic charge transfer pathways to the acidic center of the dyes (positively polarized carbonyl group) and consequently red shifts occurs.

Comparing the electronic visible absorption spectra of the acyclic merocyanine dyes (5a, b) with those of the bis acyclic merocyanine dyes (6a, b) 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 (2). The second factor is increasing conjugation due to increasing the number of methine units in bis acyclic merocyanine dyes (6a, b) related to the former acyclic merocyanine dyes (5a, b) by two methine unit, Scheme (1).

Comparing the electronic visible absorption spectra of the cyclic merocyanine dye (7) with those of the bis cyclic merocyanine dye (8) declared that the latter dye has bathochromically shifted bands related to the former one. 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 dye molecule in correspondance to one electronic charge transfer pathways inside the former dye molecule, Scheme (2). The second factor is increasing conjugation due to increasing the number of methine units in bis cyclic merocyanine dye (8) related to the former cyclic merocyanine dye (7) by one methine unit, Scheme (1).

3. Conclusion

From the above discussed results we could conclude that:

1. The electronic visible absorption spectra of the synthesized acyclic (3a-e), (4a, b), bis acyclic (5a-e), (6a, b), cyclic (7) and bis cyclic (8) merocyanine dyes in 95 % ethanol solution underwent displacements to give bathochromic shifted and/or hypsochromic shifted bands accompanied by increasing and/or decreasing the intensity of the absorption bands depending upon the following factors:

a. Presence of electron donating and / or electron attracting groups in the dyes molecules in the order of: electron donating group dyes > electron attracting group dyes.

b. Increasing π-delocalization conjugations in the dyes molecules in the order of: Ph dyes > H dyes.

c. Increasing the number of the basic centers inside the dyes molecules, in the order of: Hydantoin dyes > COOEt, $COCH_3$ dyes

d. 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.

e. Increasing and/or decreasing conjugation due to increasing and/or deceasing number of the methine units inside the dyes structure, in the order of: more methine units dyes > less methine units dyes.

2. The intensity of the colour of the synthesized acyclic (bis acyclic) and cyclic (bis cyclic) merocyanine dyes can be related to suggested two mesomeric electronic transitions structures (A) and (B) produsing a delocalized positive charge over the conjugated chromophoric group system of the dyes, Scheme (2)**.**

4. Experimental

4.1. 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. ^{1}HNMR spectra were accomplished using Varian Gemini-300 MHz NMR Spectrometer (Cairo University). Mass Spectroscopy was recorded on Mass 1: GC2010 Shimadzu 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).

4.2. Synthesis

4.2-1. Synthesis of 3,5-dicarbaldehyde-7-phenyl-furo[(3,2-d)pyraz ole;(3',2'-d) oxazole] (2):

A mixture of 1:2 molar ratios of the compound (1), (0.01 mol, 0.25 gm) and selenium dioxide (0.02 mol, 0.22 gm) were dissolved in dioxane (50 ml). The reaction mixture was heated under reflux for 16 hrs. It was filtered off while hot to remove Selenium metal, concentrated, cooled, and then precipitated by adding cold water. The precipitated product was filtered, air dried, collected, and then recrystallized from ethanol. The data are shown in Table (1).

4.2-2. Synthesis of 5-carbaldehyde-7-phenyl-furo[(3,2-d)pyrazole; (3',2'-d) oxazole-3(1)-acyclic merocyanine dyes (3a-e):

A mixture of equimolar ratios (0.01 mol) of acetaldehyde (0.06 gm), acetone (0.07 gm), acetophenone (0.12 gm), p-methoxyacetophenone (0.15 gm), or p-nitroacetophenone (0.17 gm) and the dicarbaldehyde compound (2) (0.28 gm) was dissolved in ethanol (50 ml) containing piperidine (1-2 ml). The reaction mixture, was boiled under reflux for 6 hrs. and its colour changed from reddish colour to deep brown colour at the end of the refluxing time. It was filtered while hot to remove any impurities, concentrated, cooled and precipitated by adding ice-water mixture to give the acyclic merocyanine dyes (3a-e) which crystallized from ethanol. The data were given in Table (1).

4.2-3. Synthesis of 7-phenyl-furo[(3,2-d)pyrazole;(3',2'-d)oxazole-3,5(1)-bis acyclic merocyanine dyes (4a-e):

Two different methods were used to prepare these cyanine dyes:

Methode (1): A mixture of bimolar ratios (0.02 mol) of acetaldehyde (0.12 gm), acetone (0.14 gm), acetophenone (0.24 gm), p-methoxyacetophenone (0.3 gm), or p-nitroacetophenone (0.33 gm) and the diformyl compound (2) (0.01 mol, 0.28 gm) were refluxed for 6 hrs in ethanol (50 ml) containing piperidine (1 ml). The reaction mixture, which changed from brown colour to deep brown colour at the end of refluxing, was filtered while hot to remove any impurities, concentrated, cooled, neutralized with acetic acid and precipitated by adding cold water to give the bis acyclic merocyanine dyes (4a-e) which was crystallized from ethanol. The data are given in Table (2).

Methode (2): A mixture of equimolar ratios (0.01 mol) of acetaldehyde (0.06 gm), acetone (0.07 gm), acetophenone (0.12 gm), p-methoxyacetophenone (0.15 gm), or p-nitroacetophenone (0.17 gm) and the previously prepared cyclic merocyanine dyes (3a-e) (0.01 mol) (0.33 gm for 3a, 0.36 gm for 3b, 0.49 gm for 3c, 0.55 gm for 3d, 0.58 gm for 3e) were refluxed for 6 hrs in ethanol (50 ml) containing piperidine (1 ml) as a catalyst. The reacting materials were attained apermanent intense brown colour at the end of the refluxing time. It was filtered off while hot, concentrated, cooled, precipitated by adding cold water. The precipitates were collected and recrystallized from ethanol to give the same bis cyclic merocyanine dyes obtained by route (1), characterized by melting points, mixed melting points, same visible, IR and ^{1}H-NMR spectral data, Table (2).

4.2-4. Synthesis of 5-carbaldehyde-7-phenyl-furo[(3,2-d)pyrazole; (3',2'-d)oxazole-3[2(3)] acyclic merocyanine dyes (5a, b):

An equimolar ratios (0.01 mol) of ethylacetoacetate (0.13 gm) or acetylacetone (0.1 gm) and the 3,5-dicarbaldehyde compound (2) (0.28 gm) were heated under reflux for 6 hrs in ethanol (50 ml) containing piperidine (1-2 ml). The reaction mixture, which changed from red colour to deep brown colour at the end of refluxing, was filtered while hot to remove any impurities, concentrated, cooled, precipitated by adding cold water. The precipitates were filtered off, dried and crystallized from ethanol to give the acyclic merocyanine dyes (5a, b). The data are listed in Table 3.

4.2-5. Synthesis of 7-phenyl-furo[(3,2-d)pyrazole;(3',2'-d)oxazole-3,5[2(3)]-bis acyclic merocyanine dyes (6a, b):

Two different methods were used to prepare these cyanines:

Methode (1): A mixture of bimolar ratios (0.02 mol) of ethylacetoacetate (0.25 gm) and acetylacetone (0.2 gm) and unimolar ratios of the diformyl compound (2) (0.01 mol, 0.28 gm) was refluxed for 6 hrs in ethanol (50 ml) as solvent containing piperidine (1 ml) as a catalyst. The reaction mixture, which changed from brown colour to deep brown colour at the end of refluxing, was filtered while hot to remove any impurities, concentrated, cooled, neutralized with acetic acid and precipitated by adding cold water to give the bis acyclic merocyanine dyes (6a, b) which was crystallized from ethanol. The data are given in Table 3.

Methode (2): A mixture of equimolar ratios (0.01 mol) of either ethylacetoacetate (0.13 gm) or acetylacetone (0.1 gm) and the previously prepared acyclic merocyanine dyes (5a, b) (0.01 mol) (0.39 gm for 5a, 0.36 gm for 5b) were refluxed for 6 hrs in ethanol (50 ml) containing piperidine (1 ml) as catalyst. The reacting materials were attained apermanent intense brown colour at the end of the refluxing time. It was filtered off while hot, concentrated, cooled, and precipitated by adding water. The precipitates were collected and recrystallized from ethanol to give the same bis cyclic merocyanine dyes obtained by route (1), characterized by melting points, mixed melting points, same visible, IR and ^{1}H-NMR spectral data, Table 3.

4.2-6. Synthesis of 5-carbaldehyde-7-phenyl-furo[(2,3-d)pyrazole;(3',2'-d) oxazole-3(4)-cyclic merocyanine dye (7):

Equimolar ratios of hydantoin (0.01 mol, 0.11 gm) and the diformyl compound (2) (0.01 mol, 0.3 gm) were heated under reflux in ethanol (50 ml) and presence of piperidine (1-2 ml) for 6 hrs and attained deep brown colour at the end of refluxing. The reaction mixture was filtered off on hot, concentrated, cooled, and precipitated by adding ice-water mixture. The separated cyclic merocyanine dye (7) was filtered off, washed with water, dried and crystallized from ethanol. The data were recorded in Table 3.

4.2-7. Synthesis of 7-phenyl-furo[(3,2-d)pyrazole;(3',2'-d)oxazole-3, 5(4)-bis cyclic merocyanine dye (8):

Two different methods were used to prepare these cyanine dyes:

Methode (1): Bimolar ratios of hydantoin (0.02 mol, 0.2 gm) were heated under reflux with unimolar ratios of the diformyl compound (2) (0.01 mol, 0.3 gm) in ethanol (50 ml) and presence of piperidine (1 ml) for 6 hrs. The reaction mixture attained reddish violet permanent colour at the end of the refluxing time. It was filtered off on hot, concentrated, cooled, neutralized with glacial acetic acid and precipitated by adding ice-water mixture. The separated bis cyclic merocyanine dye (8) was filtered, washed with water, dried and recrystallized from ethanol. The results are listed in Table 3.

Methode (2): A mixture of equimolar ratios of hydantoin (0.01 mol) (0.11 gm) and the previously prepared cyclic merocyanine dye (7) (0.01 mol) (0.36 gm) was boiled under reflux for 6 hrs in ethanol (50 ml) containing piperidine (1 ml) as a catalyst. The reacting materials were attained apermanent intense brown colour at the end of the refluxing time. It was filtered off while hot, concentrated, cooled and precipitated by adding cold water. The precipitates were collected and recrystallized from ethanol to give the same bis cyclic merocyanine dyes obtained by route (1), characterized by melting points, mixed melting points, same visible, IR and ^{1}H-NMR spectral data, Table 3.

4.3. Visible spectra 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 ($1x10^{-3}$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.

5. Conflict of interest

There is no conflict of interest.

6. Acknowledgement

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Appendix

Table 1:Characterization of the prepared compounds 2, (3a-e).

Comp No.	Nature of products			Molecular formula (M.Wt)	Analysis%						Absorption spectra in 95%ethanol	
	Colour	yield %	MP C°		Calculated			Found			λmax(nm)	ε_{max} (mol^{-1}.cm^2)
					C	H	N	C	H	N		
2	Deep reddish brown	50	110	$C_{14}H_7N_3O_4$(281)	59.79	2.49	14.95	59.77	2.45	14.91	…….	…….
3a	Deep violet	41	145	$C_{16}H_9N_3O_4$(307)	62.54	2.93	13.68	62.52	2.9	13.63	440, 460, 590	9570, 10330, 5620
3b	Deep violet	45	130	$C_{17}H_{11}N_3O_4$(321)	63.55	3.43	13.08	63.53	3.42	13.02	390, 470, 600	15420, 8780, 4860
3c	Deep violet	43	155	$C_{22}H_{13}N_3O_4$(383)	68.93	3.39	10.97	68.91	3.35	10.95	400, 450, 480, 510, 610	15030, 8540, 9320, 8470, 5050
3d	Deep violet	47	120	$C_{23}H_{15}N_3O_5$(413)	66.83	3.63	10.17	66.79	3.61	10.13	470, 490, 530, 620	8340, 9920, 7740, 5230
3e	Deep violet	42	125	$C_{22}H_{12}N_4O_6$(428)	61.68	2.8	13.08	61.65	2.77	13.03	450, 500, 580	9340, 7180, 5120

Table 2:Characterization of the prepared compounds (4a-e).

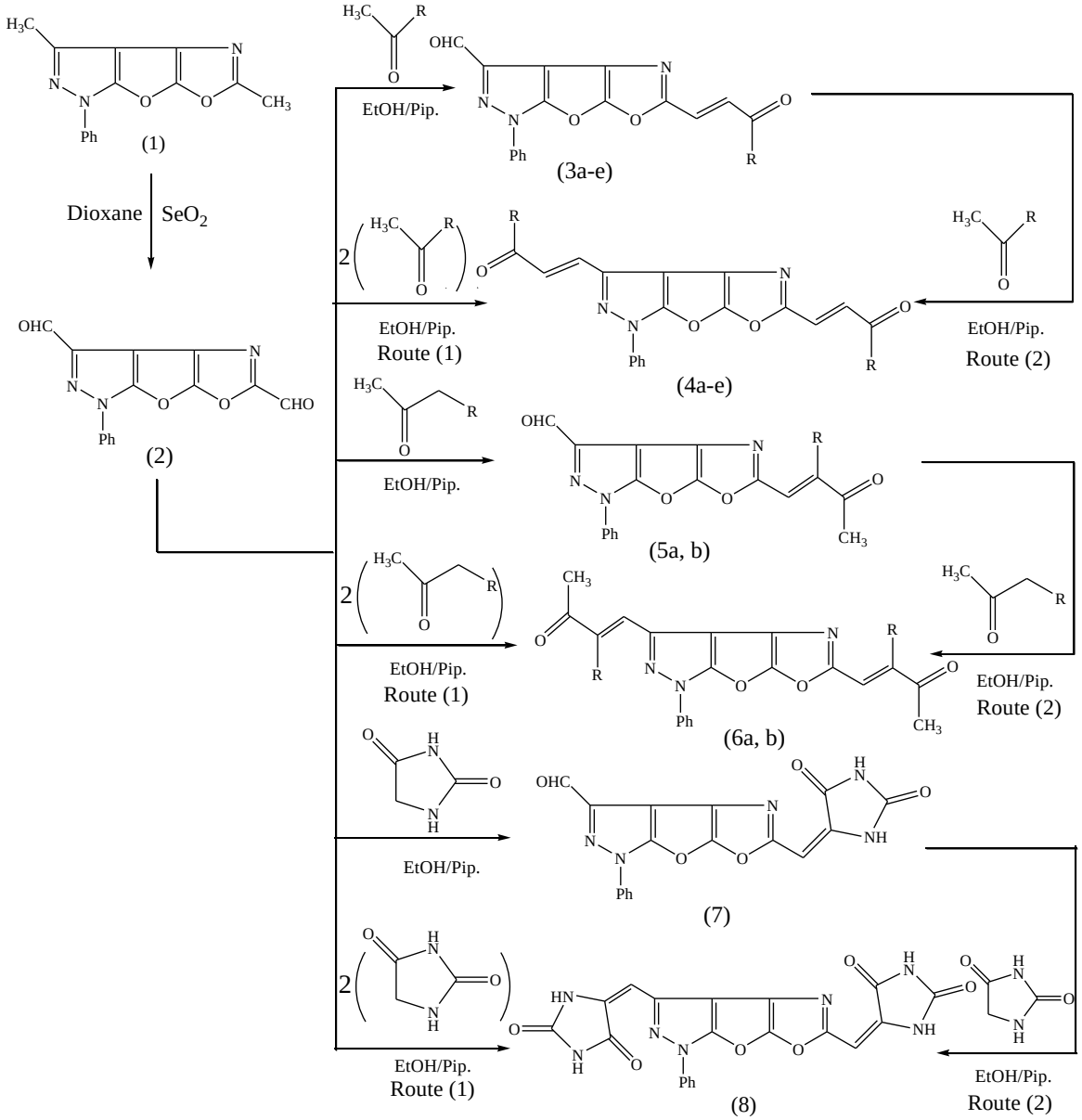
Comp No.	Nature of products			Molecular formula (M.Wt)	Analysis%						Absorption spectra in 95%ethanol	
	Colour	yield %	MP C°		Calculated			Found			λmax(nm)	ε_{max} (mol^{-1}.cm^2)
					C	H	N	C	H	N		
4a	Deep violet	46	115	$C_{18}H_{11}N_3O_4$(333)	64.86	3.3	12.61	64.81	3.28	12.59	390, 450, 470, 600	15200, 9050, 9700, 4660
4b	Deep violet	44	150	$C_{20}H_{15}N_3O_4$(361)	66.48	4.16	11.63	66.45	4.12	11.61	470, 520, 610	9700, 8490, 4990
4c	Deep violet	48	140	$C_{30}H_{19}N_3O_4$(485)	74.23	3.92	8.66	74.21	3.89	8.62	490, 530, 620	9850, 8480, 5160
4d	Deep violet	45	160	$C_{32}H_{23}N_3O_6$(545)	70.46	4.22	7.71	70.44	4.19	7.68	500, 540, 630	9890, .7780, 5390
4e	Deep violet	43	135	$C_{30}H_{17}N_5O_8$(575)	62.61	2.96	12.17	62.58	2.94	12.13	440, 460, 490, 590	8150, 9530, 8000, 5030

Table 3:Characterization of the prepared compounds (5a, b), (6a, b), 7 and 8.

Comp No.	Nature of products			Molecular formula (M.Wt)	Analysis%						Absorption spectra in 95% ethanol	
	Colour	yield %	MP C°		Calculated			Found			λmax(nm)	ε_{max} (mol^{-1}.cm^2)
					C	H	N	C	H	N		
5a	Reddish violet	56	135	$C_{20}H_{15}N_3O_6$(393)	61.07	3.82	10.69	61.03	3.8	10.65	420, 440, 480, 580	7720, 10370, 7750, 5530
5b	Reddish violet	59	150	$C_{19}H_{13}N_3O_5$(363)	62.81	3.58	11.57	62.79	3.55	11.52	430, 460, 490, 590	9490, 10530, 8850, 5340
6a	Reddish violet	57	140	$C_{26}H_{23}N_3O_8$(505)	61.78	4.55	8.32	61.73	4.51	8.31	440, 490, 590	9720, 7940, 5210
6b	Reddish violet	60	155	$C_{24}H_{19}N_3O_6$(445)	64.72	4.27	9.44	64.71	4.22	9.41	430, 460, 500, 600	8340, 9520, 7800, 4900
7	Reddish violet	62	160	$C_{17}H_9N_5O_5$(363)	56.2	2.48	19.28	56.18	2.45	19.24	450, 470, 500, 600	7200, 8700, 7700, 5080
8	Reddish violet	64	170	$C_{20}H_{11}N_7O_6$(445)	53.93	2.47	22.02	53.91	2.44	22.01	450, 480, 510, 610	135

Table 4. IR and ^{1}H NMR **(Mass)** Spectral Data of the Prepared Compounds (2), (3a), (4a), (5b), (6b), (7) and (8)

Comp. No.	IR Spectrum (KBr, Cm^{-1})	^{1}H NMR Spectrum (DMSO, δ); & (Mass data).
2	699, 748 (monosubstituted phenyl). 1031, 1116, 1170 (C—O—C cyclic). 1301, 1362 (C—N). 1493, 1405 (C=N). 1601 (C=C). 1714 (CHO).	6.9-8.3 (m, 5H, aromatic). 10.8 (b, 2H, 2CHO). M^+: 281
3a	691, 756 (monosubstituted phenyl). 1119 (C—O—C cyclic). 1363 (C—N). 1497, 1443 (C=N). 1600 (C=C). 1713 (CHO).	5.2 (b, 2H, 2 —CH=). 6.8-8.2 (m, 5H, aromatic). 9.5 (b, 2H, 2CHO).
4a	650, 691, 756 (monosubstituted phenyl). 1145 (C—O—C cyclic). 1362 (C—N). 1497, 1443 (C=N). 1598 (C=C). 1712 (CHO).	5.2 (b, 4H, 4 —CH=). 7-8.2 (m, 5H, aromatic). 10.5 (b, 2H, 2CHO).
5b	690, 755 (monosubstituted phenyl). 1116 (C—O—C cyclic). 1362 (C—N). 1495, 1445 (C=N). 1598 (C=C). 1714 (C=O).	1.1-2.4 (m, 6H, $2CH_3$ of acetyl). 5.5 (b, 1H, 1 —CH=). 6.9-8.2 (m, 5H, aromatic). 9.5 (b, 1H, CHO).
6b	647, 690, 755 (monosubstituted phenyl). 1120, 1162 (C—O—C cyclic). 1312, 1363 (C—N). 1496, 1447(C=N). 1598 (C=C). 1715 (C=O).	0.8-2.4 (m, 6H, $2CH_3$ of position 5). 3-4 (m, 6H, $2CH_3$ of position 3). 7-8.2 (m, 5H, aromatic).
7	635, 692, 754 (monosubstituted phenyl). 1067 (C—O—C cyclic). 1365 (C—N). 1495, 1440 (C=N). 1597 (C=C). 1717 (C=O). 3424 (NH).	1.4-2.4 (m, 1H, NH of position 1 in hydantoin ring). 3-3.9 (m, 1H, NH of position 3 in hydantoin ring). 4.6-5.4 (m, 1H, —CH=). 6.9-8.2 (m, 5H, aromatic). 10.0 (s, 1H, CHO).
8	634, 722, 754 (monosubstituted phenyl). 1067, 1198 (C—O—C cyclic). 1494, 1434(C=N). 1600 (C=C). 1707, 1779 (C=O). 3404 (NH).	1.4-2.4 (m, 2H, 2NH of position 1 in hydantoin ring). 3-4.0 (m, 2H, 2NH of position 3 in hydantoin ring). 4.6-5.4 (m, 2H, 2 —CH=). 6.8-8.2 (m, 5H, aromatic).

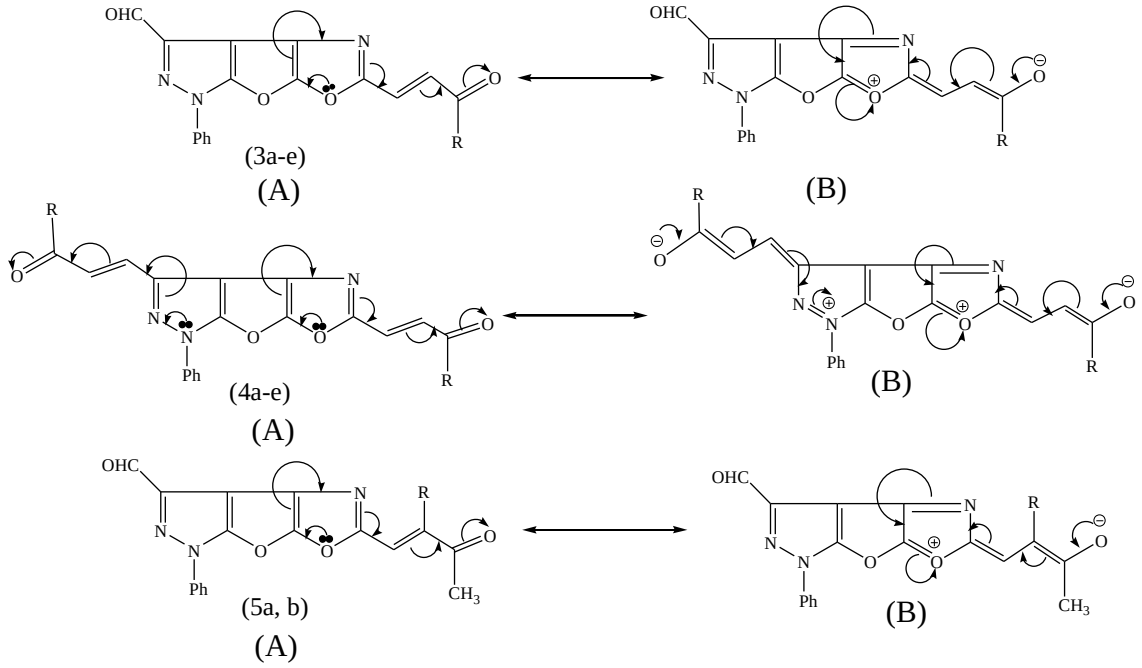


Scheme (1)

Synthesis Strategy of the prepared compounds (2), (3a-e), (4a-e), (5a, b), (6a, b), (7), and (8).

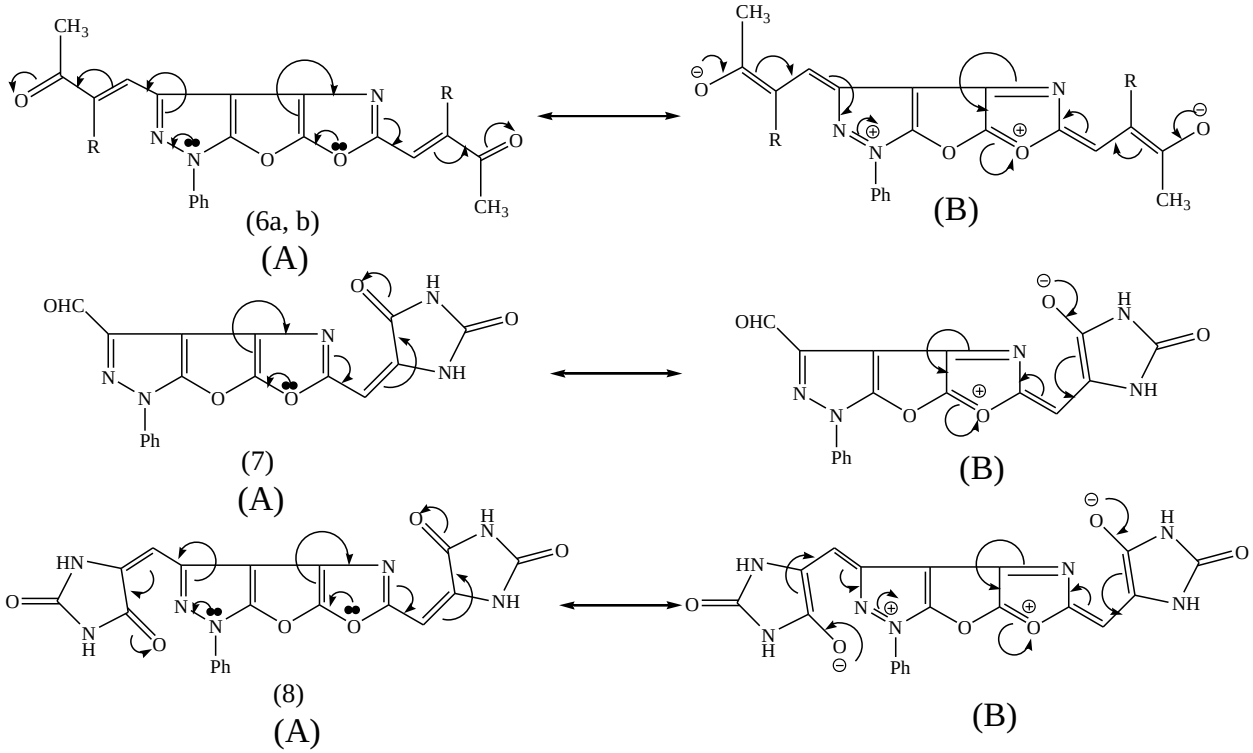
Substituents in scheme (1):

(3a-e), (4a-e): R = H (a), CH_3 (b), Ph (c), C_6H_4.p.OCH_3 (d), C_6H_4.p.NO_2 (e).
(5a, b), (6a, b): R = COOEt (a), $COCH_3$ (b)



Scheme (2)

Colour intensity and / or the electronic charge transfer pathways illustration of the synthesized acyclic merocyanine dyes (3a-e), (4a-e), (5a, b).



Scheme (2) continue

Colour intensity and / or the electronic charge transfer pathways illustration of the synthesized acyclic merocyanine dyes (6a, b) and cyclic merocyanine dyes (7), (8).