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Synthesis and Photosensitization Evaluation of Some Novel Polyheterocyclic Cyanine Dyes

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Abstract

New polyheterocyclic compound, namely 4-methyl-6-oxo-2-phenyl-furo[(3,2-d)pyrazole; (3,2-d) imidazole] was prepared and oriented to synthesis of some novel monomethine cyanine dyes, dimethine cyanine dyes and mono/di- mixed methine cyanine dyes. The electronic visible absorption spectra of all the synthesized cyanine dyes were investigated in 95% ethanol solution to evaluate their photosensitization properties. Structural identification was carried out via the elemental analysis, visible spectra, mass spectrometry, IR and ^{1}H NMR spectroscopic data.

Keywords: cyanine dyes, synthesis, photosensitization, monomethine cyanine dyes, dimethine cyanine dyes, mixed methine cyanine dyes.

Introduction

Cyanine dyes [1–14] are a class of organic heterocyclic dyes, which have long captured the interest of the scientific community. This is because the class of cyanine dyes has proved to be particularly useful in a diverse and a broad area of science, technology and engineering. Their uses and applications includes but not limited to color and non color (black and white) photography, in high energy laser and digital image storage, analytical reagents over a wide range of pH of media, indicators for solvent polarity, in biological and biomedical use as molecular probes and as fluorescent dyes commonly used for DNA visualization assays. In addition, cyanine dyes [15–28] are widely used as optical recording materials, thermal writing display, laser printers, laser filters, absorptivity and antimicrobial efficiency, for probing lipophilic environments, halophobic pockets of enzymes and components of supramolecular structures.

Taking into account and consideration the above significant benefits of cyanine dyes, in this research paper we prepared new photosensitizers cyanine dyes as new synthesis contribution and spectroscopic investigation in this field and may be used and/or applied in any of the wide mentioned application field of cyanine dyes, particularly as photographic sensitizers in photosensitive material industry, as probes for determining solvent polarity in solution chemistry, and/or as indicators in operations of acid/base titrations.

Experimental

1. General:

All the melting points of the prepared compounds are measured using Electrothermal A9100 melting point 15V, 45W apparatus (Electrothermal®, UK), Chemistry department, Faculty of Science (Aswan University, Egypt) and are uncorrected. The elemental analysis was carried out at the Microanalytical Center of Cairo University by an automatic analyzer Vario EL III (Elementar GmbH, Germany). IR-spectra were measured with a FT/IR 4100 (Jasco Analyt. Instr., Japan), Cairo University. ^{1}H NMR spectra were accomplished using Varian Gemini-300 MHz NMR Spectrometer (Gemini BV, Netherlands), Cairo University. Mass Spectroscopy was recorded on Mas 1: GC-2010 Shimadzu Spectrometer (Shimadzu, Japan), Cairo University. Electronic visible absorption spectra were carried out on a Visible Spectrophotometer, Spectro 24 RS (Labomed Inc, USA), Chemistry department, Faculty of Science (Aswan University).

2. Synthesis:

2.1. Synthesis of 4-methyl-6-oxo-2-phenyl-furo [(3,2-d) pyrazole, (3,2-d) imidazole] (3).

A mixture of equimolar ratios (0.01 mol) of hydantoin (imidazoliol-2,4-dione) (1) and 4-bromo-3-methyl-1-phenyl-5-pyrazolone (2) was dissolved in ethanol (30 ml) containing pyridine (10-20 ml). The reaction mixture was heated under reflux for 6–8 hrs and changed its colour from reddish to deep brown at the end of refluxing. It was filtered while hot to remove any impurities and precipitated by ice water mixture. The product were collected, dried and crystallized from ethanol. The results are listed in Table (1).

2.2. Synthesis of 1-methyl-2-phenyl-furo [(3,2-d) pyrazole, (3,2-d) imidazole]-6[2(4)]-monomethine cyanine dyes (4a–c).

Equimolar ratios (0.01 mol) of compound (3) and ethyl iodide quaternary salts of α-picoline, quinaldine γ-picoline were dissolved in ethanol (30 ml) containing few mls of piperidine (1–2 ml). The reaction mixture was heated under reflux for 3–5 hrs and attained colours from brown to violet at the end of refluxing. The reaction mixtures were filtered on hot to remove unreacted materials, cooled and poured in ice water mixture. The precipitated products were filtered, washed with water, dried, collected and crystallized from ethanol. The data are shown in Table (2).

2.3. Synthesis of 4-formyl-6-oxo-2-phenyl-furo [(3,2-d) pyrazole, (3,2-d) imidazole] (5).

A pure crystallized sample of (3) (0.01 mol) and selenium dioxide were heated under reflux in equimolar ratios (0.01 mol), in dioxane (30 ml) for 16–18 hrs. The reaction mixtures were filtered on hot to remove selenium metal and the filtrate was cooled and precipitated by ice water mixture. The precipitated products were filtered, dried, collected, and crystallized from ethanol to give the 4-carbaldehyde compound (5). The data are given in Table (2).

2.4. Synthesis of 6-oxo-2-phenyl-furo [(3,2-d) pyrazole, (3,2-d) imidazole]-4[2(4)]-dimethine cyanine dyes (6a–c).

A mixture of equimolar ratios (0.01 mol of compound (5) and N-iodoethane quaternary salts of α-picoline quinaldine γ-picoline were heated under refluxed in ethanol (30 ml) containing few mls of piperidine (1–2 mls) for 3–5 hrs. The reaction mixtures, which attained colours from deep brown to deep violet at the end of refluxing, was filtered. While hot to remove any impurities, cooled and precipitated by ice water mixture. The precipitated products were filtered, washed with water several times, dried, collected and crystallized from ethanol. The data are registered in Table (2).

2.5. Synthesis of 2-phenyl-furo [(3,2-d) pyrazole, (3,2-d) imidazole]-4[2(4)]di-6[2(4)]mono- mixed methine cyanine dyes (7a–c).

To different routes are employed to prepare these cyanine dyes:

Route 1: Piperidine (1–2 mls) was added to an ethanolic solution (30 ml) of (5) (0.01 mol) and bimolar ratio of 1-ethyl (α-picolinium, quinaldinium, γ-picolinium) iodide salts (0.02 mol). These mixtures were heated under reflux for 8 hrs and changed its colours from brown to deep violet colours at the end of refluxing. It was filtered off while hot, concentrated to half its volume, cooled and poured in ice water mixture. The precipitated dyes were filtered, washed with water, and crystallized from ethanol. The data are summarized in Table (2).

Route 2: Equimolar ratios (0.01 mol) of the dimethine cyanine dyes (6a–c) and iodoethane quaternary salts of α-picoline, quinaldine and/or γ-picoline were dissolved in ethanol (20 ml), to which piperidine (1–2 mls) was added. The reaction mixture was refluxed for 6 hrs exhibiting permanent intense violet colour at the end of refluxing. It was filtered while hot, concentrated, cooled and precipitated by adding cold water and ice mixture. The precipitates were collected dried and crystallized from ethanol to give the same dyes obtained by the route (1) characterized by melting points, mixed melting points, same IR and ^{1}H NMR spectral data, Table (2).

3. Photosensitization evaluation:

The electronic visible absorption spectra of the prepared cyanine dyes were examined in 95% ethanol solution and recorded using 1 cm Q_z cell on Visible Spectrophotometer, Spectro 24 RS (Labomed Inc., USA). A stock solution ($1{\cdot}10^{-3}$ *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.

Results and discussion

1. Synthesis:

An equimolar ratios of hydantoin (imidazoliol-2,4-dione) (1) and 4-bromo-3-methyl-1-phenyl pyrazole-5-one (2) were reacted in ethanol containing pyridine and achieved 4-methyl-6-oxo-2-phenyl-furo[(3,2-d) pyrazole; (3,2-d) imidazole] (3) as new polyheterocyclic starting material compound, Scheme (1), Table (1).

Reaction of (3) and iodoethane quaternary salts of α-picoline, quinaldine and/or γ-picoline in equimolar ratios in ethanol as organic solvent and piperidine as a basic catalyst gives the 6[2(4)]monomethine cyanine dyes (4a–c), Scheme (1), Table (1).

Selenium dioxide oxidation of (3) in dioxane as solvent resulted the 4-carbaldehyde compound (5), Scheme (1), Table (2). Subsequent reaction of (5) and 1-ethyl (α-picolinium, quinaldinium and/or γ-picolinium) iodide quaternary salts in equimolar ratios, in ethanol catalyzed by piperidine produced the 4[2(4)]-dimethine cyanine dyes (6a–c), Scheme (1), Table (2).

Reaction of 1:2 molar ratios of (5) and 2(4)-methyl quaternary salts of α-picoline, quinaldine and/or γ-picoline in ethanol containing few mls of piperidine achieved the 6[2(4)]*mono*-4[2(4)]*di*-mixed methine cyanine dyes (7a–c), Route (1), Scheme (1), Table (2).

Chemical confirmation takes place for the mixed methine cyanine dyes (7a–c) via the route (2) by reactions of the previously prepared dimethine cyanine dyes (6a–c) with iodoethene quaternary salts of α-picoline, quinaldine and/or γ-picoline in equimolar ratios in ethanol as organic solvent and piperidine as a basic catalyst to give the same mixed methine cyanine dyes (7a–c), prepared by the route (1), characterized by the melting point, mixed melting points, same IR and ^{1}H NMR spectral data, Scheme (1) Route (2), Table (2).

The structure of the prepared compounds was confirmed by elemental analysis, Tables (1) and (2), visible spectra, Tables (1) and (2), mass spectrometry, Table (3), IR [29] and ^{1}H NMR [30] spectroscopic data, Table (3).

2. Photosensitization evaluation:

Photosensitization evaluation of the prepared cyanine dyes was carried out via measuring their electronic visible absorption spectra in 95% ethanol solution. The dyes are thought to be better photosensitizers when they absorb light at longer wavelength bands (bathochromic shifted and/or red shifted bands). Consequently the photosensetization of the dyes decreases when they absorb light at shorter wavelength bands (hypsochromic shifted and/or blue shifted bands).

The electronic visible absorption spectra of the monomethine cyanine dyes (dimethine cyanine dyes) 4a–c (6a–c) in 95% ethanol solution represented bands in the visible range of 400–514 nm (405–520 nm). The positions of these bands underwent displacements to give bathochromic and/or hypsochromic shifted bands depending upon the nature of the heterocyclic quaternary salts (A) and their linkage positions. So, substituting (A) = 1-ethyl pyridinium-2-yl salt in the dyes 4a (6a) by A = 1-ethyl quinolinium-2-yl salt to get dyes 4b (6b) causes the bathochromic shift band by 27 nm (30 nm) for the maximum absorption spectra band accompanied by increasing intensity of the absorption bands, Scheme (1), Table (1). This can be attributed to increasing π-delocalization conjugation in the latter dyes 4b (6b) due to the presence of quinoline ring system in comparison to pyridine ring system in the former dyes 4a (6a).

Changing the linkage positions from 2-yl salt residue to 4-yl salt residue moving from dyes 4a (6a) to dyes 4c (6c) resulted in a red shift by 4 nm (4 nm) for the maximum absorption spectra band accompanied by increasing the intensity of the absorption band, Scheme (1), Table (1). This can be related to increasing the length of π-delocalization conjugation to the quaternary nitrogen of the pyridine salt in the γ-picoline dyes 4c (6c) compared to the α-picoline dyes 4a (6a).

Additionally, the electronic visible absorption spectra of the mono/di- mixed methine cyanine dyes (7a–c) in 95% ethanol solution resulted in bands in the visible region 410–530 nm. The position of these bands and their nuclear extinction coefficients is largely effected by the type of the heterocyclic quaternary salts (A) and their linkage positions, Scheme (1), Table (2). This can be attributed to the same reasons cited before in case of the electronic absorption spectra of the monomethine cyanine dyes (3a–c) and the dimethine cyanine dyes (6a–c).

The comparison the electronic visible absorption spectra of the monomethine cyanine dyes (4a–c) with those of the dimethine cyanine dyes (6a–c) reveals that the latter dyes have bathochromic shifted bands than the former dyes. This can be related to increasing the number of methine groups between the basic center (nitrogen atom) and the acidic center (quaternary salt) in latter dyes, Scheme (1), Tables (1) and (2).

Comparing the electronic visible absorption spectra of the mono/di- mixed methine cyanine dyes (7a–c) with those of the monomethine cyanine dyes (4a–c) and/or the dimethine cyanine dyes (6a–c) showed that the former mono/di- mixed methine dyes (7a–c) have red shifted and intensified absorption bands in comparison to the latter monomethine (4a–c) and dimethine (6a–c) cyanine dyes, Scheme (1), Tables (1), (2). This can be attributed to two factors. The first factor is related to increased number of methine units in the former mixed methine cyanine dyes (7a–c) in comparison to the latter monomethine cyanine dyes (4a–c) and the dimethine cyanine dyes (6a–c). The second factor is related to the presence of two electronic charge transfer pathways inside the mixed methine cyanine dyes molecules (7a–c) in correspondence to one electronic charge transfer pathways inside the molecules of the monomethine cyanine dyes (4a–c) and the dimethine cyanine dyes (6a–c), Scheme (2).

Conclusion

From the above discussed results we could conclude that:

1. The electronic visible absorption spectra of the synthesized cyanine dyes in 95% ethanol solution underwent displacements to give bathochromic and/or hypsochromic shifted bands depending upon the following factors:

A) Types of the heterocyclic quaternary salts residue in the dyes molecules in the order of: quinaldine dyes > α-picoline dyes.

B) Linkage positions of the heterocyclic quaternary salts residue in the order of: γ-picoline dyes > α-picoline dyes.

C) Number of the methine units and/or groups in the dyes molecules in the order of: mono/di- mixed methine cyanine dyes > dimethine cyanine dyes > monomethine cyanine dyes.

D) Increasing number of the electronic charge transfer pathways inside the dyes molecule in the order of: two electronic charge transfer pathways dyes > one electronic charge transfer pathways dyes.

2. The intensity of the colours of the monomethine cyanine dyes (4a–c), the dimethine cyanine dyes (6a–c) and the mixed methine cyanine dyes (7a–c) can be attributed to two suggested mesomeric structures (A) and (B) producing a delocalized positive charge over the conjugated system, Scheme (2).

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Table (1): Characterization of the prepared compounds (3), (4a–c)

Comp. No.	Nature of products			Molecular formula (M.Wt.)	Analysis%						Absorption spectra in 95% ethanol	
					Calculated			Found				
	Colour	Yield (%)	M.p. (C°)		C	H	N	C	H	N	λ_{max} (nm)	ε_{max} ($mol^{-1}cm^2$)
3	Brown	75	290	$C_{13}H_{10}N_4O_2$ (254)	61.41	3.93	22.04	61.33	3.87	22.00	----------	----------
4a	Brown	51	155	$C_{21}H_{20}N_5OI$ (485)	51.95	4.12	14.43	51.85	4.10	14.38	400, 487	7000, 5900
4b	Violet	65	160	$C_{25}H_{22}N_5OI$ (535)	56.07	4.11	13.08	56.00	4.01	13.00	417, 514	7300, 8200
4c	Deep brown	54	180	$C_{21}H_{20}N_5OI$ (485)	51.95	4.12	14.43	51.89	4.00	14.32	405, 491	7200, 6200

Table (2): Characterization of the prepared compounds (5), (6a–c) and (7a–c)

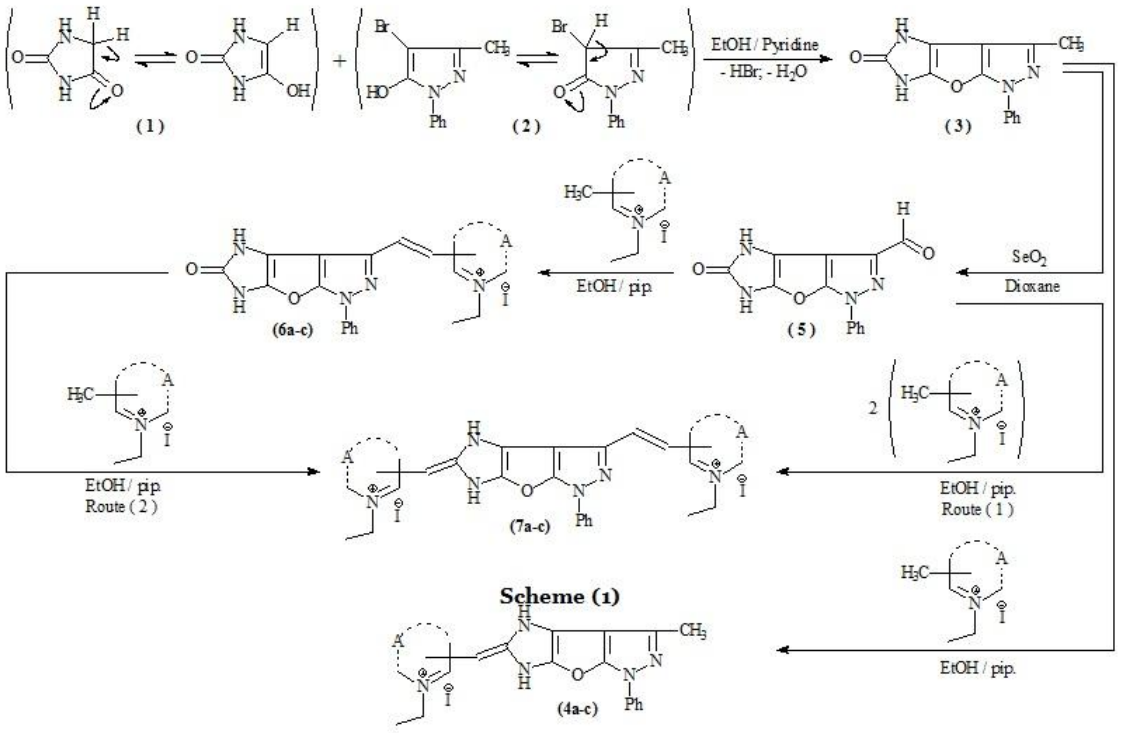
Comp. No.	Nature of products			Molecular formula (M.Wt.)	Analysis%						Absorption spectra in 95% ethanol	
					Calculated			Found				
	Colour	Yield (%)	M.p. (C°)		C	H	N	C	H	N	λ_{max} (nm)	ε_{max} ($mol^{-1}cm^2$)
5	Red	65	160	$C_{13}H_8N_4O_3$ (268)	58.20	2.98	20.89	58.16	2.81	20.70	----------	----------
6a	Brown	45	185	$C_{20}H_{18}N_5O_2I$ (499)	50.50	3.60	14.02	50.13	3.53	14.01	405, 490	1100, 7900
6b	Deep violet	63	170	$C_{25}H_{20}N_5O_2I$ (549)	54.64	3.64	12.75	54.30	3.40	12.66	420, 520	1500, 1850
6c	Deep brown	52	190	$C_{21}H_{18}N_5O_2I$ (499)	50.50	3.60	14.02	50.45	3.61	14.00	410, 494	7500, 6200
7a	Brown	61	200	$C_{29}H_{28}N_6OI_2$ (730)	47.67	3.83	11.50	47.50	3.75	11.42	410, 510	7000, 6000
7b	Deep Violet	98	195	$C_{37}H_{32}N_6OI_2$ (830)	53.49	3.85	10.12	53.11	3.20	10.00	430, 530	9000, 2100
7c	Deep Brown	53	188	$C_{29}H_{28}N_6OI_2$ (730)	47.67	3.83	11.50	47.52	3.78	11.40	420, 520	1000, 9000

Table (3): IR and ^{1}H NMR (mass) spectral data of the prepared compounds

Comp. No	IR Spectrum (KBr, cm^{-1})	^{1}H NMR Spectrum (DMSO, δ); & (Mass data)
3	588, 700 (mono substituted phenyl) 1031, 1117, 1168 (C-O-C cyclic) 1407, 1495 (C=N) 1603 (C=C) 1719 (C=O) 3437 (NH)	2.15 (s, 3H, CH_3 of position 4). 7.2 (m, 2H, 2NH) 7.4–7.8 (m, 5H, aromatic) M^+: 254
4b	624, 690 (mono substituted phenyl) 756, 810 (o.disubstituted phenyl) 1158 (C-O-C) cyclic) 1486 (C=N) 1597, 1633 (C=C) 2921, 2854 (quaternary salt) 3432 (NH)	1.4 (b, 3H, CH_3 of N-quinolinium) 2.15 (b, 3H, CH_3 of position 4) 3.5 (b, 2H, CH_2 of N-quinolinium) 7.1 (b, 2H, 2NH) 7.3-8.3(m, 12H, aromatic + heterocyclic + -CH=)
5	649, 691(mono substituted phenyl). 1029, 1055, 1130, 1170 (C-O-C cyclic) 1496, 1562 (C=N) 1597 (C=C) 1722 (C=O) 3230 (NH)	7.1 (b, 2H, 2NH) 7.2-8 (m, 5H, aromatic) 10.6 (s, 1H, CHO) M^+: 268
6b	692, 754 (mono substituted phenyl) 794, 828 (o.disubstituted phenyl) 1040, 1087, 1129, 1158 (C-O-C cyclic) 1415 (C=N) 1596 (C=C) 1715 (C=O) 2921, 2851 (quaternary salt) 3428 (NH)	1.2 (b, 3H, CH_3 of N-quinolinium) 3.3 (b, 2H, CH_2 of N-quinolinium) 6.7 (b, 2H, 2NH) 7.2-8.2 (m, 13H, aromatic + heterocyclic + 2-CH=)

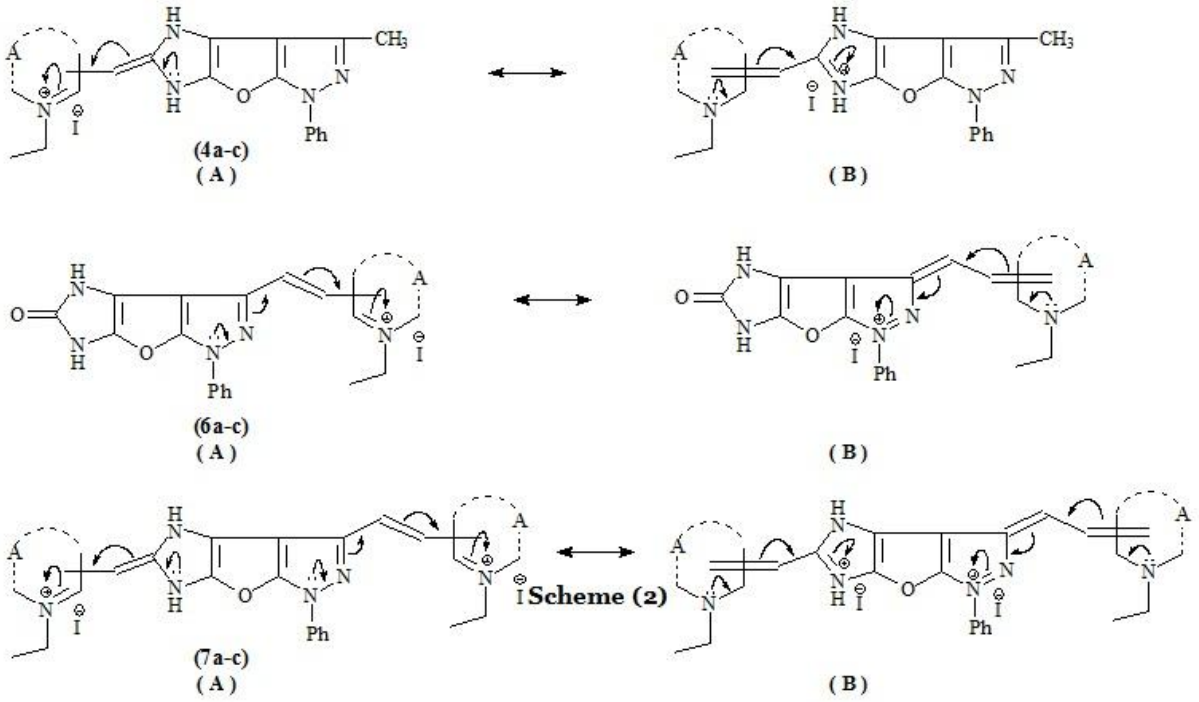
Table (3): Continue

Comp. No	IR Spectrum (KBr, cm^{-1})	^1H NMR Spectrum (DMSO, δ); & (Mass data)
7b	648, 692 (mono substituted phenyl) 753, 800 (o.disubstituted phenyl) 1085, 1154 (C-O-C cyclic) 1495, 1463 (C=N) 1595 (C=C) 2923, 2852 (quaternary salt) 3428 (NH)	1.2 (b, 3H, CH_3 of N-quinolinium of position 4) 1.6 (b, 3H, CH_3 of N-quinolinium of position 6) 2.3 (m, 2H, CH_2 of N-quinolinium of position 6) 3.3 (b, 2H, CH_2 of N-quinolinium of position 4) 6.7 (b, 2H, 2NH) 7.3-8.2 (m, 20H, aromatic + heterocyclic + 3 =CH-)



Scheme (1)

Substituents in Scheme (1):
(4a–c); (6a–c); (7a–c): A=1-ethyl=pyridinium-2-yl salt (a); 1-ethyl-quinolinium-2-yl salt (b); 1-ethyl pyridinium-4-yl salt (c).



Scheme (2)