



Fundamentals in the chemistry of cyanine dyes: A review



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Applications of cyanine dyes

ABSTRACT

In this review paper, some of the important fundamentals in the chemistry of cyanine dyes were explained. This include topics like structure and resonance forms of cyanine dyes, naturally occurring cyanine dyes, different classes of cyanine dyes and formation mechanisms of cyanine dyes. This covers methine cyanine dyes, apocyanine dyes, styryl cyanine dyes (hemicyanine dyes), aza-styryl cyanine dyes) aza-hemicyanine dyes, merocyanine dyes (acyclic merocyanine dyes and cyclic merocyanine dyes) squarylium cyanine dyes (aromatic squarylium cyanine dyes and heterocyclic squarylium cyanine dyes), spectral sensitization evaluation of cyanine dyes, solvatochromic evaluation of cyanine dyes, halochromic evaluation of cyanine dyes, cyanine dyes for CD-R and DVD-R, cyanine dyes as fluorescent labels for nucleic acid research, mechanisms of dimethine cyanine dyes and mechanisms of apocyanine dyes. In addition, in the introduction section of this review paper some light is focussed on some important uses and applications of cyanine dyes. This special and/or specific type of collective review in the fundamentals, principles, knowledge and/or the understanding of cyanine dyes chemistry has been paid little attention and is lacking in the chemistry literature.

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1. Introduction

More and more attention have been paid to the chemistry of cyanine dyes [1–20]. This is because the multiplicity uses and applications of these dyes in several fields of science, technology engineering, pharmacology and medicine. Such as spectral sensitizers for silver halide emulsion in photographic industry for coloured and non coloured (black and white) films, as acid–base indicators in analytical chemistry, as anti-tumor and/or anti-cancer agents in medicine, as bactericidal and fungicidal agents in pharmaceutical industry, for nucleic acid and protein detection, for labeling of biomolecules, in laser technology, in organic solar cells, in optical recording disks [CD-R and DVD-R media (stabilized cyanine disks are often rated with an archival life of 75 life years or more)], in determination of carbon–carbon bond length, in textile industry, as corrosion inhibitors, as electrophotographic photoreceptors, in printing inks, as synthetic drugs, as inhibitors for cell growth and division in many biological process, as cosmetic ingredients, as reagents in biomedicine, as indicator for solvent polarity, as suitable model systems to understand and/or study the colour of

organic compounds (studies on cyanine dyes have greatly enhanced our understanding of delocalized electronic structures and colour chemistry), as photorefractive materials, dyes for polymers, in laser printers, in histological staining, as intercalating agents, as hormonal effects on plant growth, in photodynamic therapy (PDT) and in semiconductor materials industry. The developments of cyanine dyes synthesis and their applications in photographic and non-photographic multidisciplinary areas are growing continuously, significantly and rapidly. Certainly, this will make the present and the future of cyanine dyes chemistry effective, fruitful and very bright. The positive future and continuous importance of these dyes in modern science and advanced technologies is reflected by a number of so many numerous publications in the synthesis, characterization and applications of cyanine dyes in the present time [21–40].

Because cyanine dyes have multiple uses and applications in a diverse and broad area of science, technology, engineering, pharmacology and medicine, this review paper might be very interesting and useful for the large heterogenous community groups of chemists, biologists, physicists, biotechnologists, pharmacologists and medical scientists. In addition, this paper review will be informative, useful, and an excellent key reference work for chemists and researchers who are keen to have the fundamental

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understanding, principles and knowledge of cyanine dyes chemistry. Besides, this paper review can be used and will be most valuable for students, particularly for the post graduate students in the field of heterocyclic and cyanine dyes chemistry. Furthermore, this paper review is recommended to anyone interested in the subject, to chemistry libraries and also for the personal bookshelves of every organic heterocyclic and cyanine dyes chemist.

2. Structure and resonance forms of cyanine dyes

The true cyanine dyes have two nitrogen heterocyclic rings joined by a conjugation chain of carbon atoms as in Fig. 1.

Typical examples for a cyanine dye based on such structure are pinacyanol (2) and kryptocyanine (3) dyes [41], Fig. 2.

Two resonance structures (2a) and (2b), (3a) and (3b) of the pinacyanol and kryptocyanine dyes are shown in Fig. 2, respectively. Between these two structures the actual dye is a resonance hybrid [42]. p. Toluene sulphonate, alkyl or any groups can take place of N-ethyl groups. For the preparation of cyanine dyes quaternary salts with active (acidic) methyl groups at 2 and/or 4 positions are usually used, such as the quaternary salts of 2-methyl pyridine (α -picoline/2-picoline), 2-methyl quinoline (quinaldine), 4-methyl pyridine (γ -picoline/4-picoline) and/or 4-methyl quinoline (lepidine). To make increasing for the reactivity (acidity) of the methyl group, other heterocyclic quaternary salts than 2(4)-methyl pyridine and/or 2(4)-methyl quinoline can be used, such as the quaternary salts of 2-methyl thiazole, 2-methyl bcnzothiazole, 2-methyl oxazole, 2-methyl benzoxazole, 2-methyl selenazole and/or 2-methyl benzoselenazole [43]. Also, for the preparation of cyanine dyes quaternary salts with active (acidic) hydrogen atom at 4 and/or 1 positions are usually used, such as the quaternary salts of pyridine, quinoline and/or isoquinoline [43].

3. Naturally occurring cyanine dyes [44–47]

Since their accidental discovery, cyanine dyes have been identified as colourants in natural products. These natural dyes were first observed by Wyler in the late 1960s and by Musso in the late 1970s. These dyes were confirmed to contain a similar feature; a pentamethinium cyanine (dicarbocyanine) chromophore substituted with two chiral end groups derived from L- α -amino acids. Betanin, which is responsible for the red-violet colour of the red beet, *Beta vulgaris*, exhibits a visible absorption at 537 nm. The orange-red fungus dye musca-aurin I, is found in the toadstool fly agaric *Amanita muscaria*, with an absorption maximum at 475 nm, Fig. 3.

4. Different classes of cyanine dyes [48–53]

4.1. Methine cyanine dyes

Cyanine dyes are classified according to the number of methine ($-\text{CH}=\text{}$) groups in the chain between the two ring systems and the nature of the ring moiety present. If one methine group is present

($n = 0$ in Fig. 1) the dye is monomethine cyanine dyes or simple cyanine dyes, e.g. Quinoline blue dye (4) and Ethyl red dye (5), Fig. 4. The dye with 3 methine groups ($n=1$ in Fig. 1) is classified as trimethine cyanine dyes or carbocyanine dyes, e.g. pinacyanol dye (2) and kryptocyanine dye (3), Fig. 2.

If 5 methine groups is present ($n=2$ in Fig. 1), the dyes are known as pentamethine cyanine dyes or dicarbocyanine dyes, and the dyes with 7 methine groups ($n=3$ in Fig. 1) are known as heptamethine cyanine dyes or tricarbocyanine dyes, and so on.

4.2. Apocyanine dyes

This type of cyanine in which the two nuclei are directly linked and have no methine groups between the two rings are known as apocyanines which despite their importance have received little attention. The only known compounds of these dyes are the red erythroapocyanine (6) and its isomeric yellow component xanthoapocyanine (7), obtained as a mixture by the action of alkali on a highly concentrated alcoholic solution of quinoline alkyl halide, Fig. 5.

4.3. Styryl cyanine dyes (hemicyanine dyes)

These types of compounds resemble cyanine dyes having two nitrogen atoms connected by a chain of conjugated double bonds, but differ from them as one nitrogen atom is not part of a heterocyclic nucleus. The first salt of this type was prepared in 1920 through the condensation of quinaldine or lepidine quaternary salt with p-dimethylaminobenzaldehyde in the presence of piperidine as a catalyst and ethanol as a solvent, whereby styryl cyanines (8) and (9) were obtained, Fig. 6.

4.4. Aza-styryl cyanine dyes (Aza-hemicyanine dyes and/or Aza-cyanine dyes)

Aza-styryl cyanine dyes can be prepared by the reaction of quaternary salt of α -picoline, γ -picoline, quinaldine and/or lepidine with p-nitroso phenol, α -nitroso- β -naphthol and/or β -nitro- α -naphthol, in basic alcohol solution, Fig. 7.

Also, aza-styryl cyanine dyes can be prepared by the reaction of 2(4)-formyl quaternary salts of pyridine, and quinoline with aniline and/or substituted aniline in basic alcohol solution, Fig. 8.

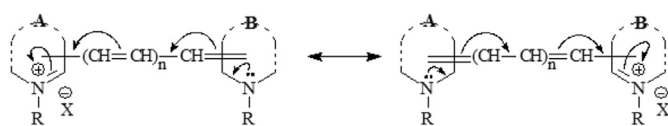
4.5. Merocyanine dyes

This class of compounds is very much related to cyanine dyes. They are characterised by the presence of cyclic or acyclic carbonyl group ($\text{C}=\text{O}$) which may be replaced by $\text{C}=\text{S}$. They are non-ionic compounds having the general structure which is given in Fig. 9.

Merocyanine dyes are classified according to the number of methine groups, when $n = 0$, where the two nuclei are directly linked, they are known as simple merocyanines. When $n = 1$, it is known as dimethine merocyanine, $n = 2$, it is known as tetramethine merocyanine, and $n = 3$, it is known as hexamethine merocyanine.

There are a number of compounds that can be used in the preparation of acyclic merocyanine dyes and/or cyclic merocyanine dyes like, ethylacetoacetate (acetoacetic ester), diethylmalonate (malonic ester), acetylacetone and/or malonyl urea (barbitone/barbituric acid/1,3,5-tri-H-pyrimidine-2,4,6-tri-one), hydantion (imidazolidine-2,4-dione), respectively, Fig. 10.

A representative example for acyclic merocyanine dyes and cyclic merocyanine dyes is given in Fig. 11. From this Figure we notice that acyclic merocyanine dyes are characterised by the presence of acyclic (outside ring) carbonyl group in its structure.



($n = 0, 1, 2, 3 \dots$ etc)

Fig. 1.

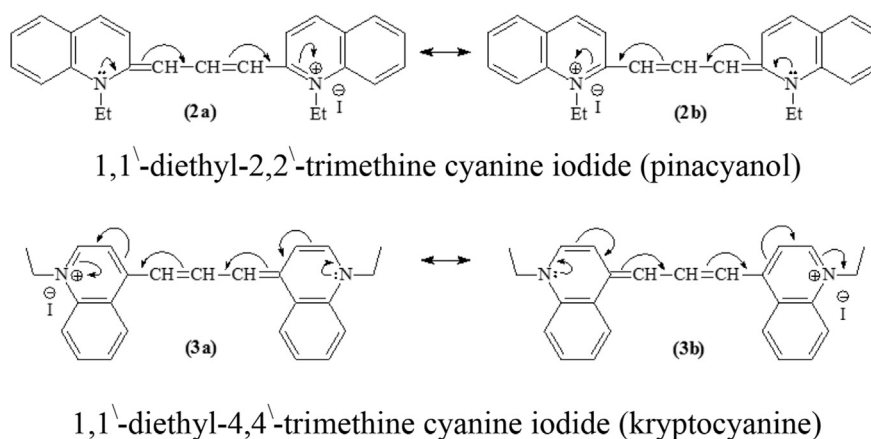


Fig. 2.

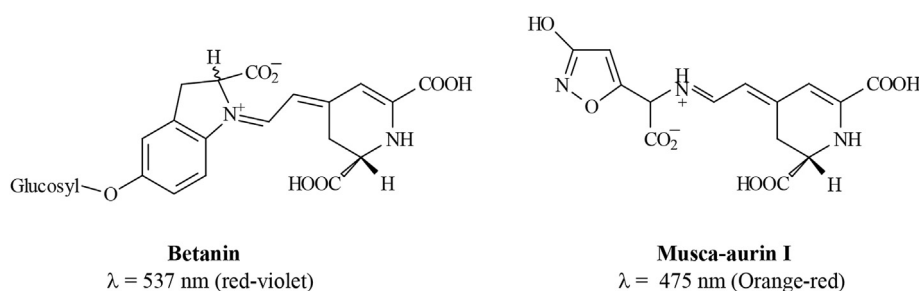


Fig. 3.

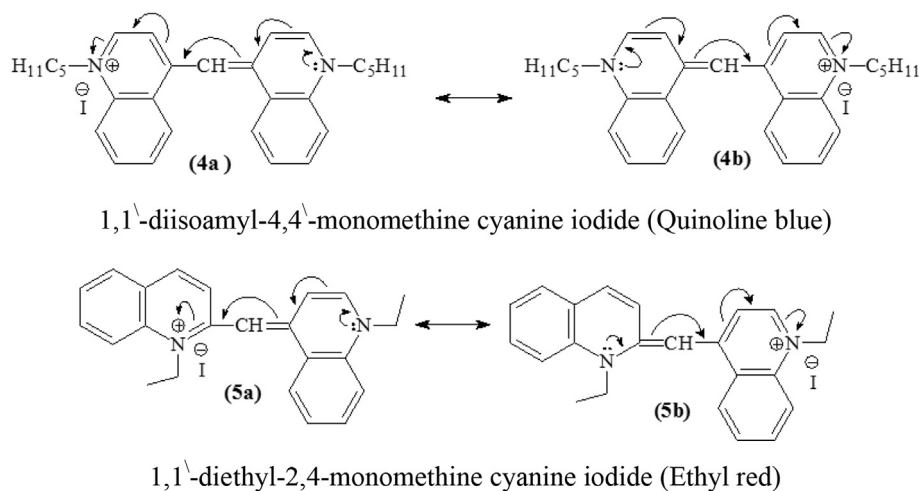


Fig. 4.

Inversely, the cyclic merocyanine dyes are characterised by the presence of cyclic (inside ring) carbonyl group in its structure, Fig. 11.

4.6. Squarylium cyanine dye

Squarylium cyanine dyes are 1,3-disubstituted compounds resulting from the condensation of one equivalent of squaric acid (3,4-dihydroxy-1,2-dioxocyclobut-3-ene) with two molar equivalents of electron donating aromatic (like aniline, N,N-dimethylaniline) or heterocyclic (like 2-methyl-indolenines, 2-

methyl-benzothiazole or 2-methyl-benzoselenazoles) methylene bases, Fig. 12.

5. Spectral sensitization, solvatochromic, and halochromic evaluation of cyanine dyes [54,55]

Spectral sensitization evaluation for any synthesized cyanine dyes can be made 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).

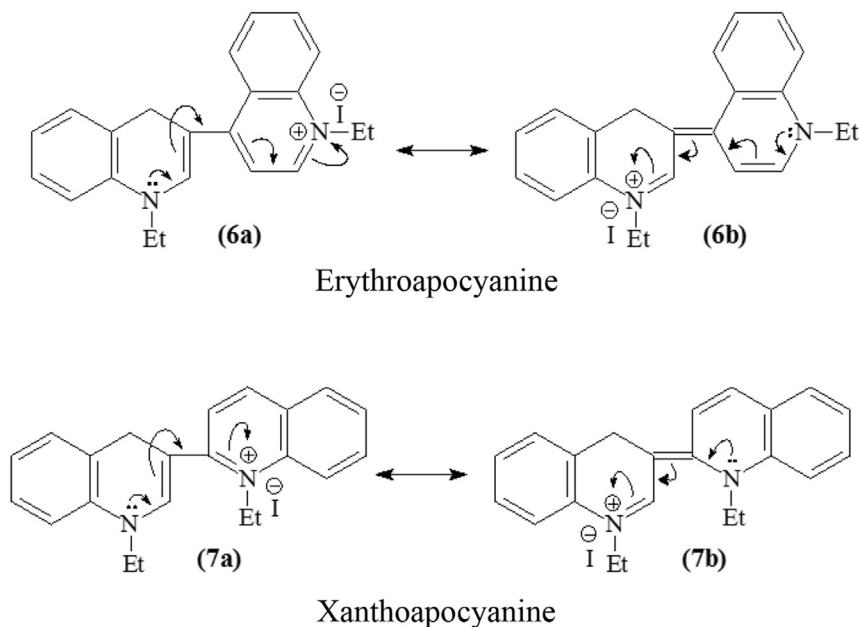


Fig. 5.

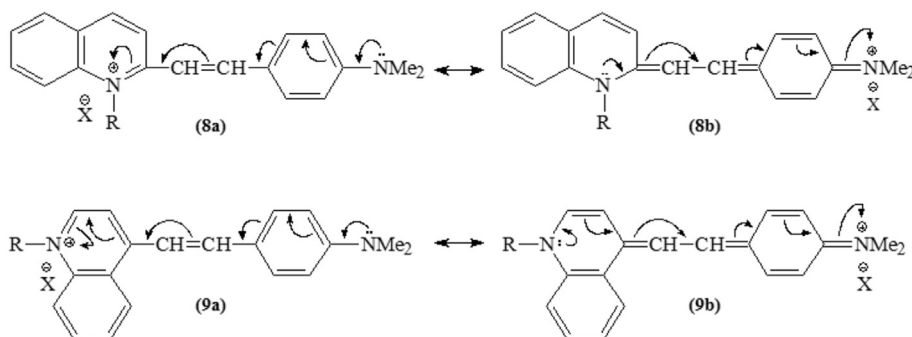


Fig. 6.

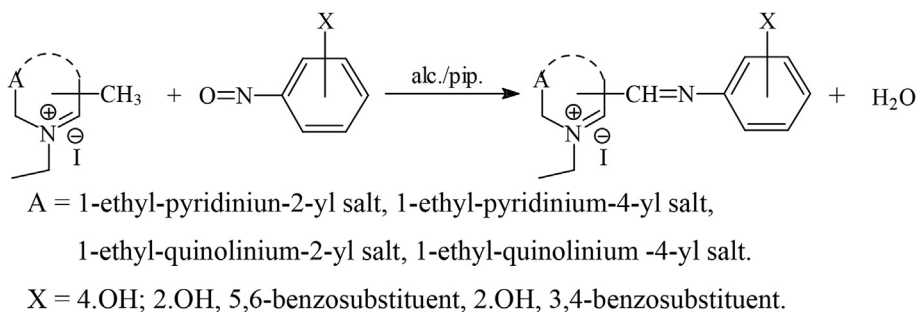


Fig. 7.

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. Spectral sensitization evaluation study is very important in the case of cyanine dyes because the extensive uses of these dyes in photographic 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.

In addition, solvatochromic evaluation for any synthesized cyanine dyes can be carried out via examining their electronic

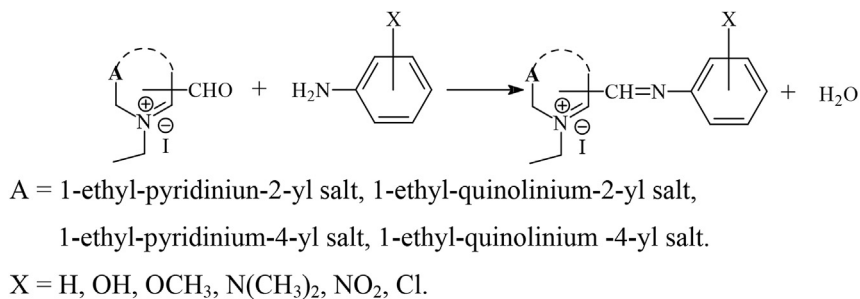


Fig. 8.

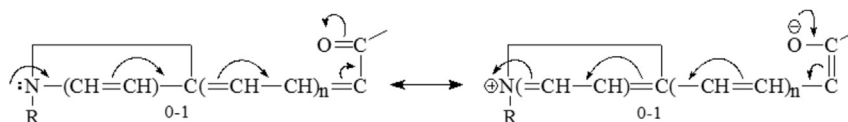


Fig. 9.

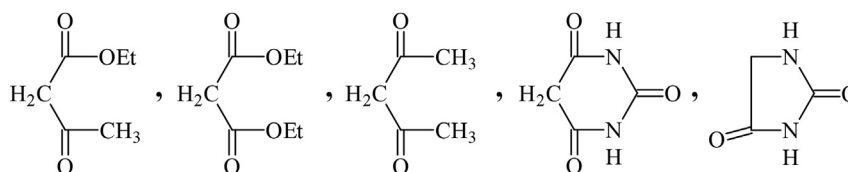


Fig. 10.

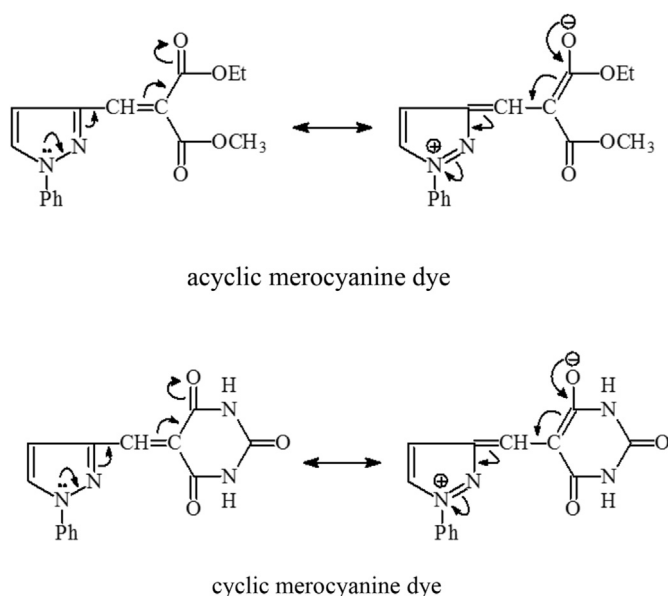


Fig. 11.

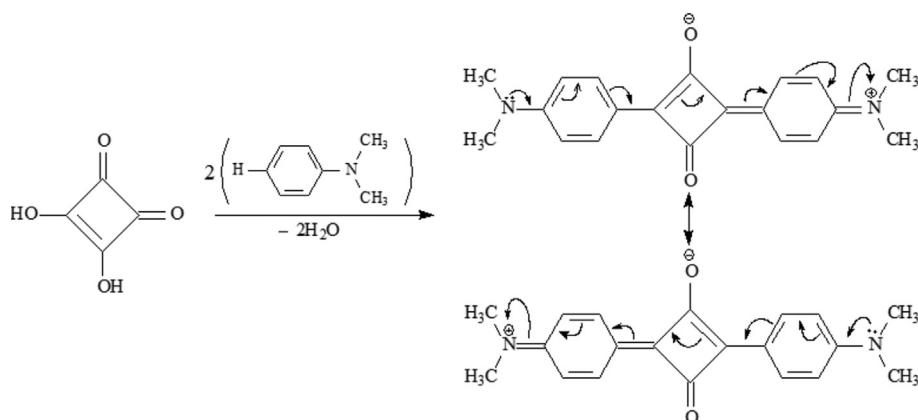
visible absorption spectra in pure solvents having different polarities. The dyes were thought to be better solvatochromic dyes when they give a remarkable positive solvatochromism and/or negative solvatochromism in these solvents. Positive solvatochromism reveals bathochromic shifted (red shifted) absorption bands with increasing solvent polarity. Inversely, negative solvatochromism discloses hypsochromic shifted (blue shifted) bands with increasing solvent polarity. This study is usually carried out to select the best solvents to use of these dyes as photosensitizers

when there are used and/or applied as photographic sensitizers in manufacturing technology of photosensitive material industry. The other important purpose of this study is to evaluate the solvatochromic properties of these dyes to may be use and/or applied as probes for determining solvent polarity in physical, physical organic and/or inorganic chemistry. Particularly, solvatochromic study is very important in the case of hemicyanine dyes because the extensive uses of hemicyanine dyes in textile industry/.

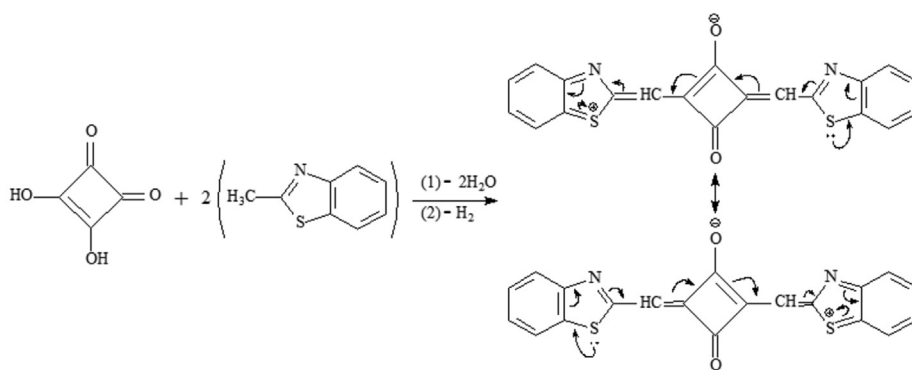
Besides, halochromic evaluation for any synthesized cyanine dyes can be determined by measuring their electronic visible absorption spectra in aqueous universal buffer solutions having varied pH values. The dyes were thought to be better halochromic dyes when they give a noticeable positive halochromism and/or negative halochromism in these buffer solutions. Positive halochromism means occurrence of a bathochromic shifted (red shifted) absorption bands with changing solution pH of the buffer solution. In contrast negative halochromism means occurrence of a hypsochromic shifted (blue shifted) absorption bands with changing the pH of the buffer solution. Halochromic evaluation study is useful study in the case of cyanine dyes in order to select a suitable pH for use of these dyes as photosensitizers. The other purpose of this study is to evaluate the halochromic properties of these dyes to may be used and/or applied as pH indicators in operations of acid/base titration in analytical chemistry.

6. Cyanine dyes for CD-R and DVD-R [56]

Since the reading and writing laser wavelength for CD-R is 780 nm, the cyanine used for this purpose is mainly pentamethine cyanine dyes. The properties of cyanine dyes play an important role in the quality of CD-R disks. The structure, such as heterocycles, substituents of the heterocycles and the counter ion, have a great effects on the absorption spectra, refractive index, reflectivity and



Aromatic squarylium cyanine dyes



Heterocyclic squarylium cyanine dyes

Fig. 12.

writing speed, which are very important parameters for cyanine dyes used as recording medium. The variation of these parameters with the structure of cyanine dyes have been discussed before. DVD-R is the next generation optical recording medium and will replace CD-R in the market. The recording density of DVD-R is 7–8 times higher than CD-R due to its shorter writing and reading laser wavelength at 630–650 nm. According with the laser wavelength, cyanines used for DVD-R is mainly trimethine cyanine dyes and hemicyanine dyes. The latest development of cyanine dyes for DVD-R disks have been reviewed before.

7. Cyanine dyes as fluorescent labels for nucleic acid research [57]

Modification of proteins, DNA and other biopolymers by labeling them with reporter molecules has become a very powerful research tool in molecular biology. In addition, there are a growing number of commercial applications of these modified biomolecules including clinical immunoassay, DNA hybridization tests, gene fusion detection tests, etc. In these techniques, a small molecule with spectral properties such as fluorescent or binding specificity, is covalently or non-covalently bound to biomolecules. The interaction of small molecules with nucleic acids giving detectable signal is a very useful method for the investigation of biological processes on the molecular level. The fluorescent dyes that either associate

selectively with macromolecules, or partition into specific sites within cells, are site-selective probes. Most of the site-selective probes are used to label cellular organelles, cytoskeletal components, DNA, RNA, nucleotides, neurotransmitters and many other biological macromolecules. The non-covalently binding labels have no fluorescence of their own, but a strong fluorescence enhancement is observed in the presence of nucleic acids.

8. Synthesis mechanisms of some cyanine dyes [51,58–60]

8.1. Mechanism of dimethine cyanine dyes

The mechanism of this reaction (Fig. 13) is suggested to proceed as follows:

The first step in this suggested mechanism is attacking of basic catalyst piperidine to the active methyl group of the quaternary salt forming the carbanion ion (a), (Fig. 14). The second step involves attacking the carbanion ion (a) to the positive center of the aldehydic carbonyl group of the pyrazole compound forming the intermediate compound (b). In the third step the intermediate compound (b) directly abstracts H proton from piperidine-forming compound (c), as intermediate compound. In the fourth step the intermediate compound (c) undergoes heat refluxing conditions to give the dimethine compound (d), Fig. 14.

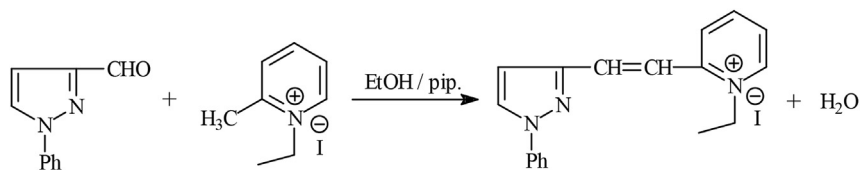


Fig. 13.

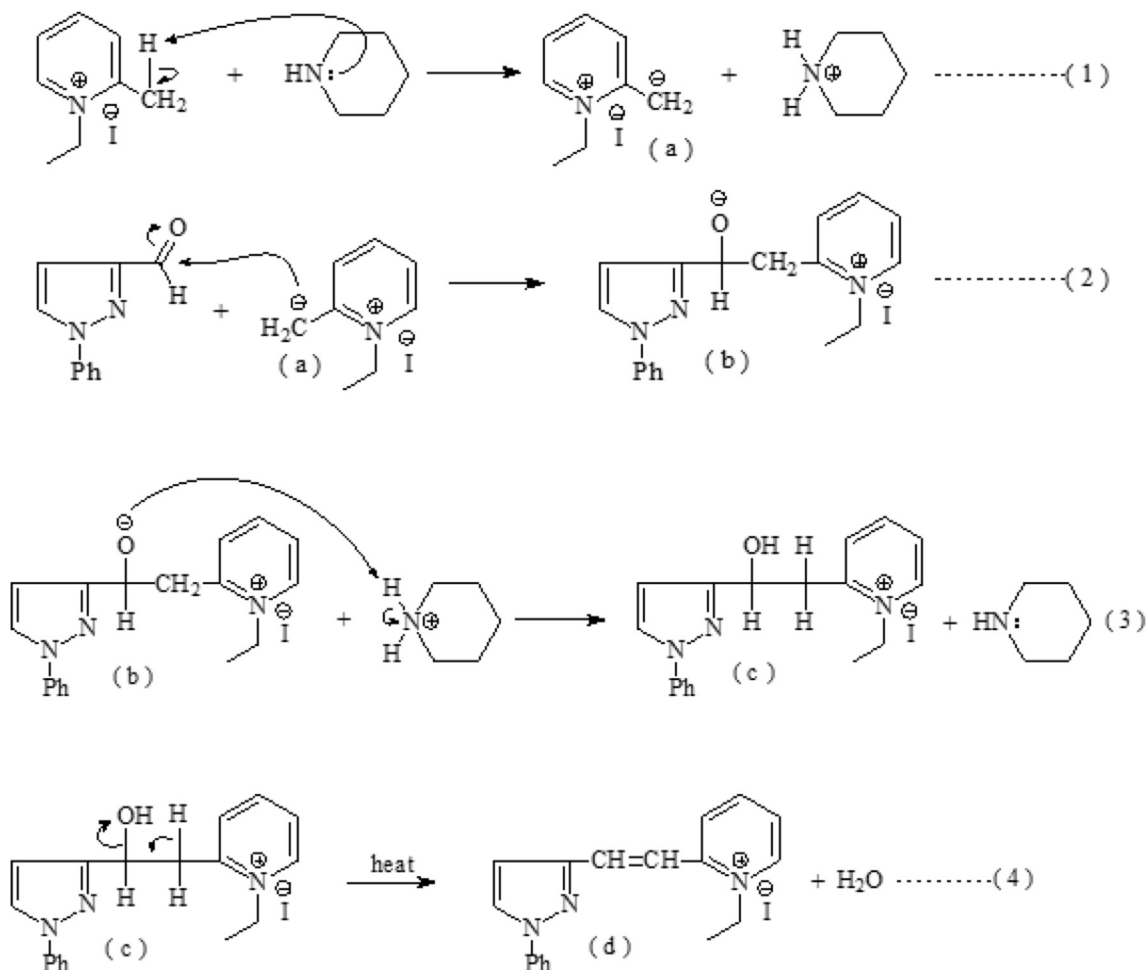


Fig. 14.

8.2. Mechanism of Apocyanine dyes

The mechanism of this reaction (Fig. 15) is suggested to proceed as follows:

The first step in this mechanism involves dehydrohalogenation of the dibromides to acetylenic derivatives, equation (1), (Fig. 16). The second step is a simple addition of the polarized amine at the acetylenic residue followed by dehydrogenation to give the apocyanine dye (E), equation (2), Fig. 16.

9. Conclusion

Following are major conclusions were drawn from this study:

- 1 The uses and applications of cyanine dyes are not limited to one and/or two research area, but it includes multiplicity

fields in science, technology, engineering, pharmacology and medicine.

- 2 The structure of most cyanine dyes is characterised by the presence of two resonance forms (two mesomeric structures). These two resonance forms have the responsibility for the intensity of the colour of cyanine dyes where they produce a delocalized positive charge over the conjugated structure system of cyanine dyes.
- 3 According to their origin and nature, cyanine dyes are classified to two main types, naturally occurring cyanine dyes (vegetable source) and pure synthetic cyanine dyes (chemical source).
- 4 Depending on their structure, cyanine dyes are classified to different classes, such as methine cyanine dyes, hemicyanine dyes, merocyanine dyes, apocyanine dyes and squarylium cyanine dyes.

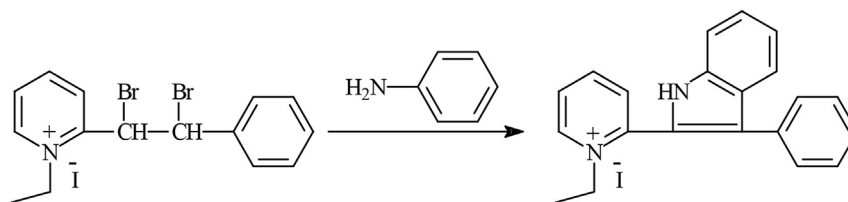


Fig. 15.

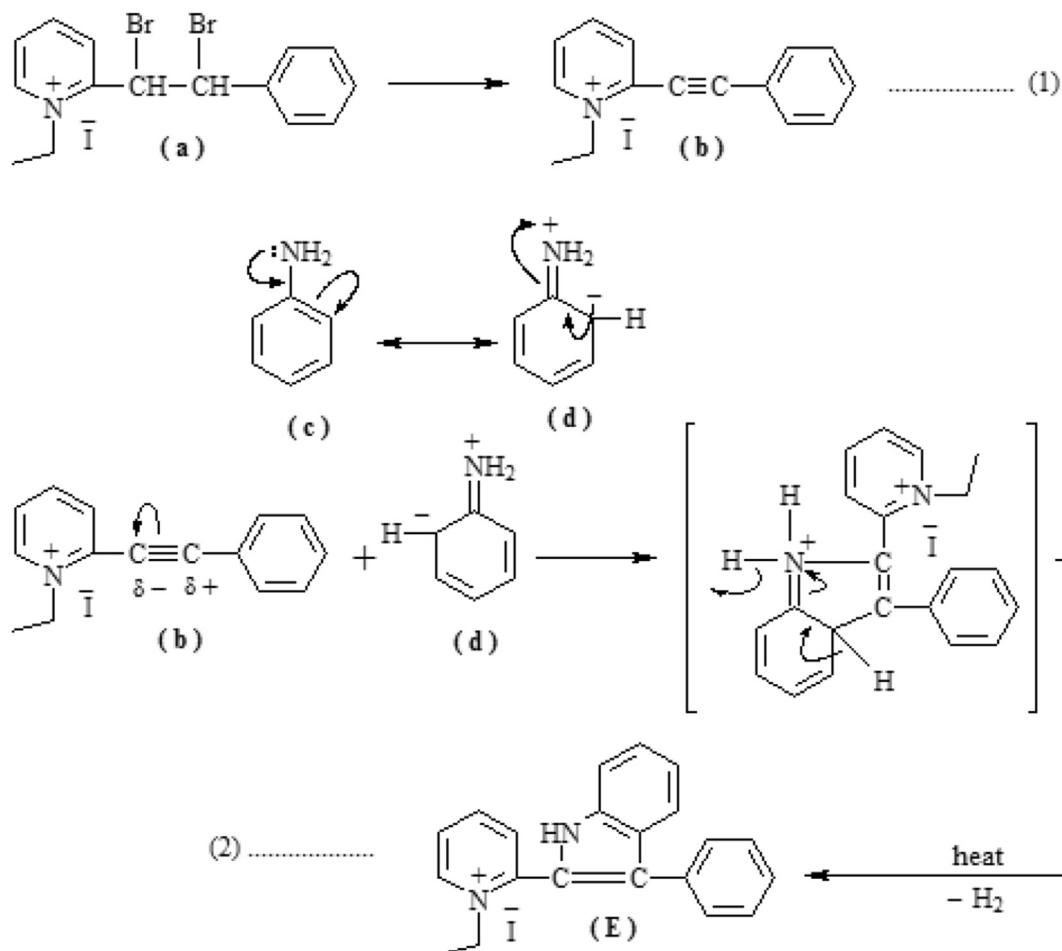


Fig. 16.

- 5 Spectral sensitization evaluation for cyanine dyes can be made by investigating their electronic visible absorption spectra in 95% ethanol solution.
- 6 Solvatochromic evaluation of cyanine dyes is carried out through examining their electronic visible absorption spectra in pure solvents having different polarities.
- 7 Halochromic evaluation of cyanine dyes can be determined by measuring their electronic visible absorption spectra in aqueous universal buffer solutions having varied pH values.
- 8 Cyanine dyes used for CD-R is mainly pentamethine cyanine dyes, since the reading and writing laser wavelength for CD-R is 780 nm. In contrast, cyanine dyes used for DVD-R is mainly trimethine cyanine dyes and hemicyanine dyes, since the reading and writing laser wavelength for DVD-R is 630–650 nm.

- 9 The techniques of cyanine dyes as fluorescent labels for nucleic acid research depends upon that a small molecule with spectral properties such as fluorescent or binding specificity, is covalently or non-covalently bound to bio-molecules. The interaction of small molecules with nucleic acids giving detectable signal is a very useful method for the investigation of biological processes on the molecular level.
- 10 Synthesis mechanisms of cyanine dyes depends on the class type of cyanine dyes. Each class have different synthesis mechanism method depending on the nature of the heterocyclic quaternary salts, catalyst used in the reaction and kind of the main heterocyclic nucleus employed in the reaction.

10. Current future developments

The current and/or the future research developments aimed to provide new, novel and/or patent review papers in the field of colour, dyes and pigments chemistry. The aimed review papers will covers and/or includes topics like the origin of colour, the relation between colour and constitutions, synthesis of dyes, properties of dyes, classification of dyes, uses and/or applications of dyes. Also, additional important topics for the current and/or the future research developments for the aimed review papers will includes methine cyanine dyes (monomethine cyanine dyes, dimethine cyanine dyes, trimethine cyanine dyes ... etc.), hemicyanine dyes (styryl cyanine dyes), merocyanine dyes (acyclic merocyanine dyes and cyclic merocyanine dyes), apocyanine dyes, monoheterocyclic cyanine dyes, biheterocyclic cyanine dyes, polyheterocyclic cyanine dyes, six membered heterocyclic cyanine dyes, five/five membered heterocyclic cyanine dyes, five/six membered heterocyclic cyanine dyes, five membered heterocyclic cyanine dyes and benz(naphth)/ five membered heterocyclic cyanine dyes.

Conflict of interest

There is no conflict of interest.

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