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REVIEW

SYNTHESIS OF DIFFERENT CLASSES OF BENZ (NAPHTH) / FIVE MEMBERED HETEROCYCLIC CYANINE DYES

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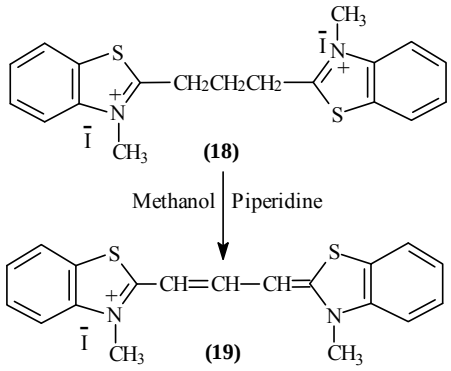
In this paper synthesis of different classese of some benz (naphth) / five membered heterocyclic cyanine dyes have been reviewed. The synthesis covers monomethine cyanine dyes (simple cyanine dyes), aza-monomethine cyanine dye (aza-cyanine dyes), trimethine cyanine dyes (carbocyanine dyes), pentamethine cyanine dyes (dicarbocyanine dyes), tetramethine cyanine dyes, heptamethine cyanine dyes (tricarbocyanine dyes), styryl cyanine dyes (hemi cyanine dyes), a cyclic merocyanine dyes, cyclic merocyanine dyes, squarylium cyanine dyes and bridged cyanine dyes. Besides, in the introduction section of this review paper some light has been focused on the uses, applications and properties of cyanine dyes. This specific type of collective review has been paid little attention and is lacking in the chemistry literature.



INTRODUCTION

Cyanine dyes[1-8] belongs to the class of complex organic compounds. These dyes exhibit large molar absorptivities and moderate quantum yields resulting in extremely bright fluorescence signals. Therefore, cyanine dyes have proven to be useful in several fields of science and technology including photography, biology, laser technology and analytical chemistry.[9-12] Some unique series of lipophilic cyanine dyes are useful for biophysical studies of lipid bilayers of cells or other artificial membranes, in potential for labeling lipid bilayers, for labeling hydrophobic pockets of lipo-proteins and for use in the aforementioned fields.[9-12]

In addition, cyanine dyes can also be used for fluorescent indicators,[13] for antihalation, antiradiation or color filter function,[14] in staining biological membranes[15] and for photorefractive materials.[16] They are also used in CD-R and DVD-R media.[17,18] The ones used are mostly green or light blue in colour, and are chemically unstable. This makes cyanine dyes discs unsuitable for archival CD and DVD use, as they can fade and become unreadable in a few years. However, recent cyanine discs contain stabilizers that slow dawn the deterioration significantly. Cyanine dyes were the earliest developed ones and the standard characteristics of CD-R were established on the basis of cyanine-based optical recording disk. So these dyes played a very important role in the development of CD-R. Cyanine dyes have a number of advantages when used as optical recording materials such as high absorption, small

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thermal conductivity and diffusivity with the possibility to form good pits configuration and high reflectivity in a laser beam wavelength. Since the writing and reproducing laser wavelength for CD-R is 780 nm, the cyanine used in this purposes is mainly pentamethine cyanine dyes.[19]

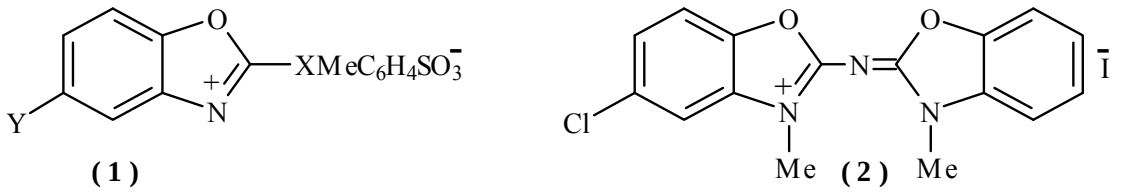
Besides, cyanine dyes are coloured organic heterocyclic dyes compounds which have a delocalized electronic structures and very intense absorption spectra bands in the visible region of the spectrum.[20-22] This strong absorption of light at particular wavelengths makes solutions of these molecules brightly coloured. The strong absorption leads to many applications of these dyes in technology. For example, these dyes are used to colour plastics, fabrics, and hair. They can also be used to filters to produce coloured light and as laser medium in medical applications.

SYNTHESIS OF DIFFERENT CLASSES OF BENZ (NAPHTH) / FIVE MEMBERED HETEROCYCLIC CYANINE DYES

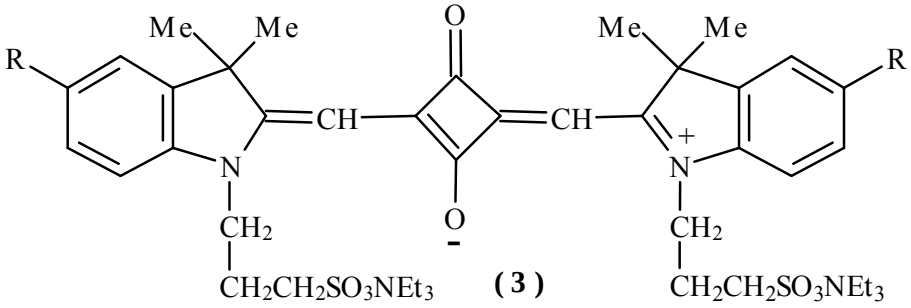
UV absorping azamonomethines containing azole ring (2) was prepared via interaction of benzoazole (1, X = NH_2, Y = Cl) and benzoazole (1, X = S Me, Y = ph) followed by treating with NaI,[23] Scheme 1.

Eight novel squarylium cyanine dyes (3, R = H, Me, OMe, F, Cl, Br, COOH, NO_2) were synthesized,[24] Scheme 2.

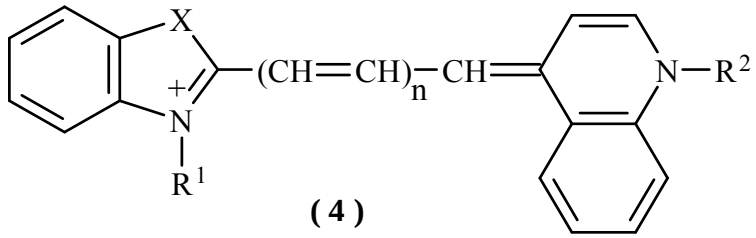
Asymmetrical cyanine dyes (4); at least one of R^1 and R^2 is a linking group; X = O, S, Se; n = 0 – 2 were obtained. For example, (4), R^1 = Me, R^2 = 5-carboxypentyl; n = 1; nitro group on the 6-position of the benzothiazolium ring were prepared,[25] Scheme 3.



Scheme 1



Scheme 2



Scheme 3

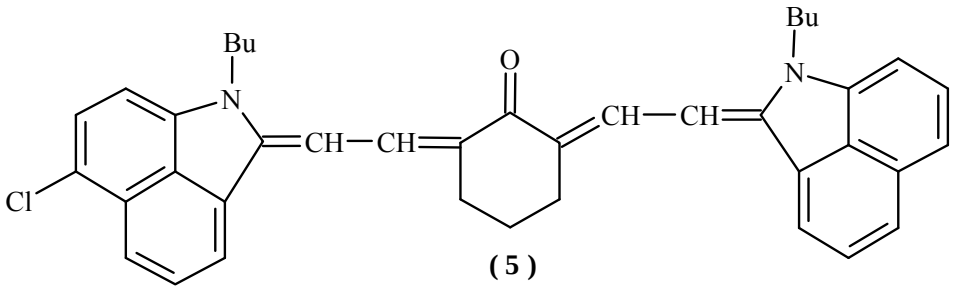
A pH-sensitive near-infrared chromophore dye (5) was prepared by Lee, Linda G. *et al.* (λ_{max} 648 nm in MeOH). This dye undergoes protonation at the oxygen atom to give a cyanine chromophore (λ_{max} 392 nm). The transition is fully reversible and depends solely on pH conditions,[26] Scheme 4.

Twenty-one butadienylene chain-substituted hemicyanine dyes (6; R = H, Cl, Br, I, Me, OMe, OEt; R^1 = H, Cl, OH) have been synthesized by the catalytic condensation of 4-dimethyl aminostyryl phenyl ketone, 4-dimethyl aminostyryl 4-chlorophenyl ketone and 4-dimethyl aminostyryl 4-hydroxyphenyl ketone with 2-methyl-benzothiazole methiodide and several 2-methyl-6-substituted benzothiazole methiodides using ethanolic DMF as solvent and piperidine as basic catalyst,[27] Scheme 5.

Trimethine cyanine dyes (7, R^1 = H, NO_2; R^2 = Me, CH_2CH_2OH, CH_2CH_2Cl; R^3 = H, NO_2) were prepared by condensation of 2-formyl methylene-3,3-dimethyl indoline with 2-cyanomethyl benzimidazoles,[28] Scheme 6.

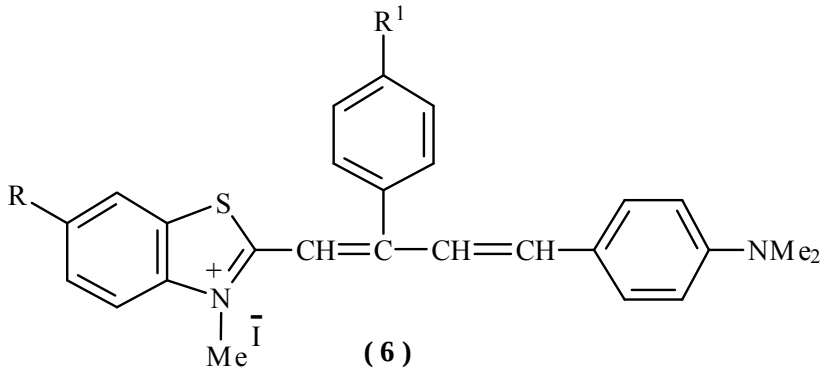
Asymmetrical trimethine cyanine dyes (8, R = Me, Et, allyl, hydroxyethyl; R^1 = H; R^2 = H, OMe; X = O, S, CH:CH, CMe_2; R^1 X = CH:CH:CH:C; A = ClO_4, Br, I) were synthesized,[29] Scheme 7.

Styryl cyanine dyes (9) containing the benz [c, d] indolium heterocycle was synthesized where R =Et, $CH_2CH{:}CH_2$; R^1 = H or R^1R^2 = $(CH_2)_3$; R^2 = Et or R^2R^3 = $(CH_2)_4$ or $(CH_2)_2O(CH_2)_2$; R^3 = Et, CH_2CH_2CN or R^3R^4 = $(CH_2)_3$; R^4 = H; R^5 = EtO, MeO, OH, or H,[30] Scheme 8.



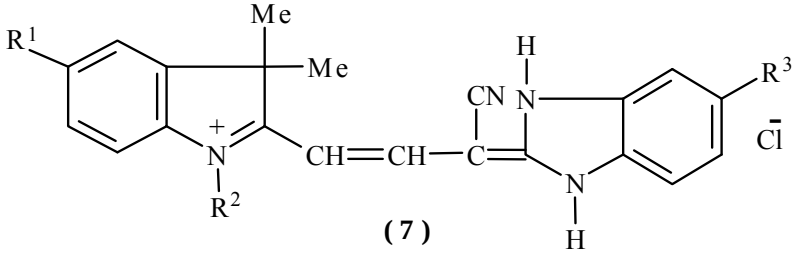
(5)

Scheme 4



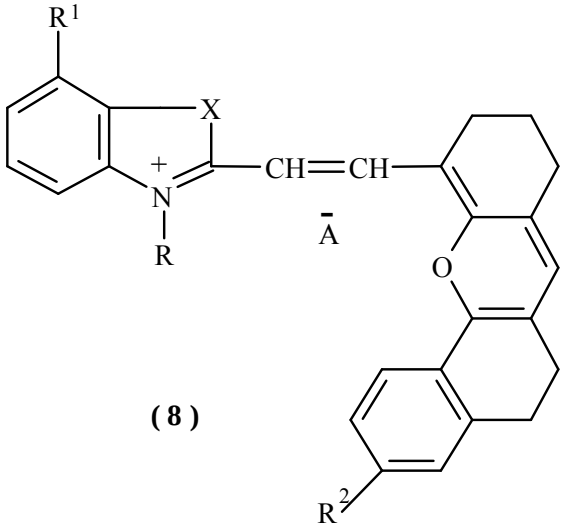
(6)

Scheme 5



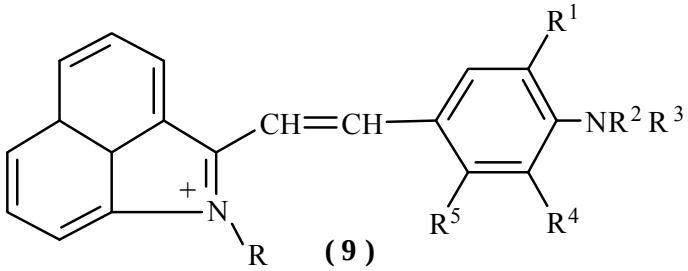
(7)

Scheme 6



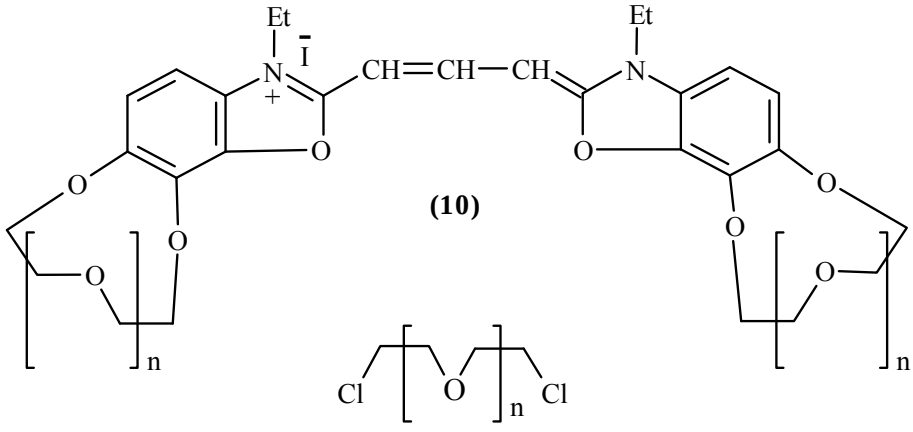
(8)

Scheme 7



(9)

Scheme 8



(10)

(11)

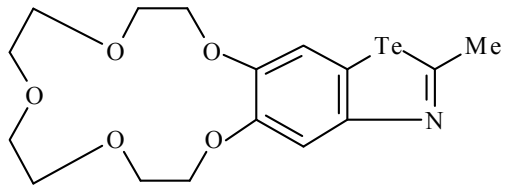
Scheme 9

A series of benzoxazole crown ether cyanine dyes (10, n = 1,2) having increased stability and photosensitivity were prepared by the Beckman rearrangement of 2,3,4-trihydroxy acetophenone oxime, cyclization of the dihydroxy methyl benzoxazole intermediate with (11, n = 1) or (11, n = 2), quaternization with EtI, and reaction with $HC(OEt)_3$,[31] Scheme 9.

Three methods for synthesing of benzotellurazole crown ether (12) are described. The cyanine dye (13) can be easily obtained by treating (12) with MeI and $CH(OEt)_3$,[32] Scheme 10.

Cyanine dyes (14; R^1 = C_{6-22}-alkyl; R^2 = H, Me, Cl, Br, alkoxy, phenoxy, mercaptoalkyl, phenylthio; X = Cl, Br, I, $MeSO_3$, $MeC_6H_4SO_3$, F_3CSO_3, BF_4,ClO_4) were synthesized,[33] Scheme 11.

Cyanine dyes (15, 16; M = Na, K; n = 1, 2; R^1, R^2 = H, SO_3M or R^1R^2 may form an annelated ring containing sulfo group (s); R^3= sulfoalkyl, carboxyalkyl, hydroxyalkyl; R^4 = carboxyalkyl, hydroxyalkyl; X = Cl, Br) were obtained for use as fluorescent markers,[34] Scheme 12.



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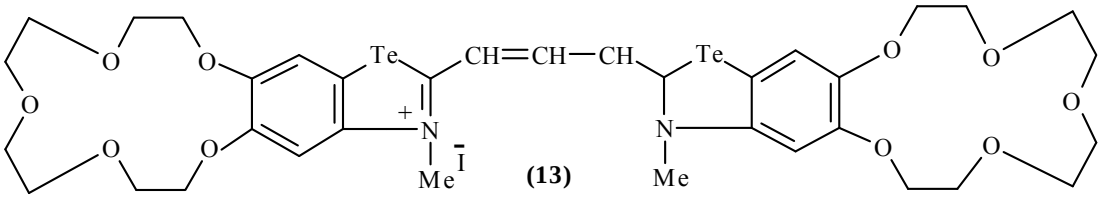
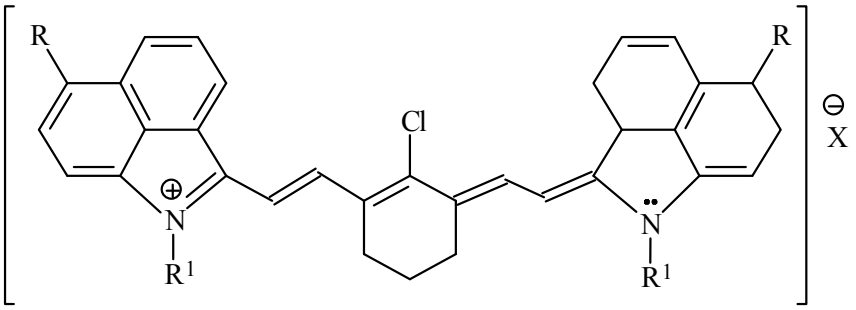


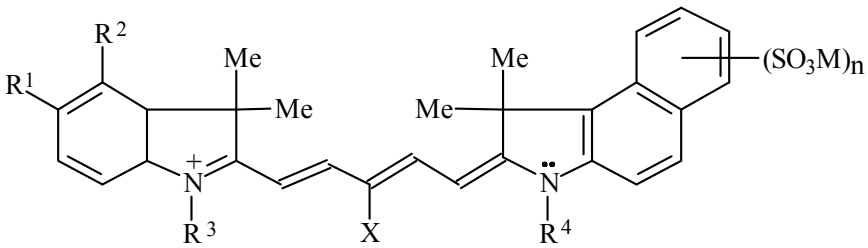
(13)

Scheme 10

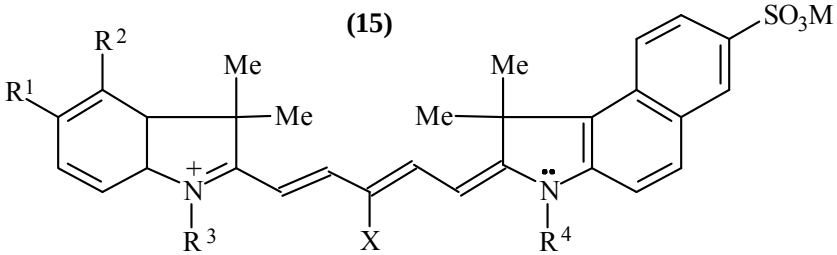


(14)

Scheme 11



(15)



(16)

Scheme 12

Asymmetrical trimethine cyanine dyes (17, R^1 = H, Me, Et; R^2,R^3 = (un) substituted C_{1-12} alkyl; Ā = halo, ClO_4^-, BF_4^-, PF_6^-, SbF_6^-, $CF_3SO_3^-$, $C_2F_5SO_3^-$, $CF_3CO_2^-$, $MeC_6H_4SO_3^-$; X = H, alkyl, alkoxy, halo, nitro, condensed benzene; Y = H, alkoxy, halo, alkyl, aryl, alkoxycarbonyl, aryloxycarbonyl, alkylamine, arylamine, alkylamide, arylamide, alkylsulfonyl, arylsulfonyl, alkoxysulfonyl, aryloxysulfonyl, nitro, cyano) were prepared,[35] Scheme 13.

Katritzky *et al.* synthesized thiacarbocyanine dye (19) by treating 1,3-bis (N-methyl-2-benzothiazolyl)propane diiodide salts (18) with two equivalents of piperidine in methanol. The oxidation presumably occurs by air,[36] Scheme 14.

Katritzky *et al.* synthesized a novel fused ring bridged cyanine dyes (20, 21, 22, 23, 24) via reactions of 1,3-bis(N-methyl-2-benzothiazolyl) propane diiodide salts (18) with 2,3-dichloro-1,4-naphthoquinone, tetrachloro-1,2- and 1,4-benzoquinone, 3,4-dichloromaleimide and 2,3-dichloro-quinoxaline,[36] Scheme 15.

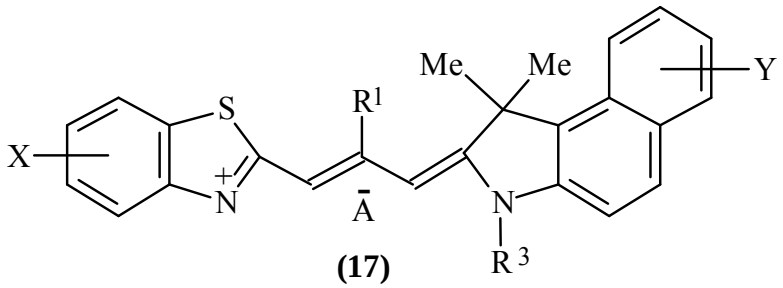
A series of substituted and/or unsubstituted heptamethine cyanine dyes were synthesized by condensation of 2,3,3-trimethyl indolenium salts with 2-chloro-1-formyl-3-hydroxymethylene cyclo-hexane or with N[5-(phenylamino)-2,4-pentadienylidene] aniline monohydrochloride,[37] Scheme 16.

Substituents in Scheme 16:

(25a – f); (26a – f); (27a – f): R = H (a); CH_3 (b); OCH_3 (c); Cl (d); NO_2 (e); 4,5-benzo (f).

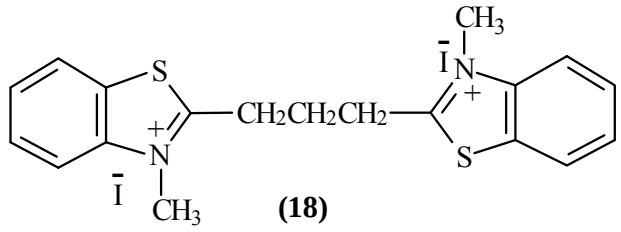
Merocyanine dyes[38] based on the pyrazolin-5-one system were synthesized by condensing 3-methyl-1-phenyl-pyrazolin-5-one with 1,3,3-trimethyl-2-methylene indolinealdehyde (Fischer's aldehyde), Scheme 17.

B. Narayan *et al.* synthesized new styryl and/or hemi cyanine dyes containing benthiazole nucleus,[39] Scheme 18.



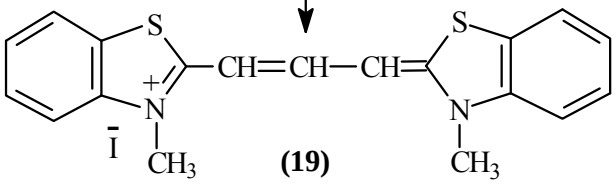
(17)

Scheme 13



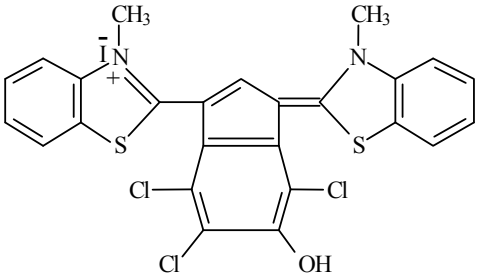
(18)

Methanol | Piperidine



(19)

Scheme 14



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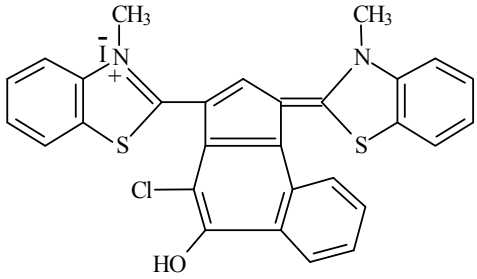
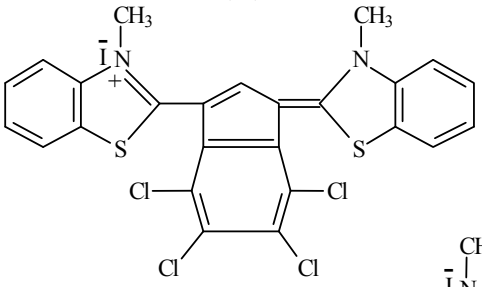
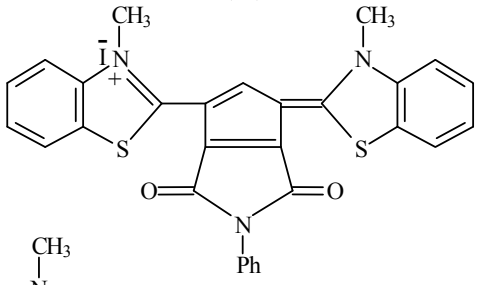


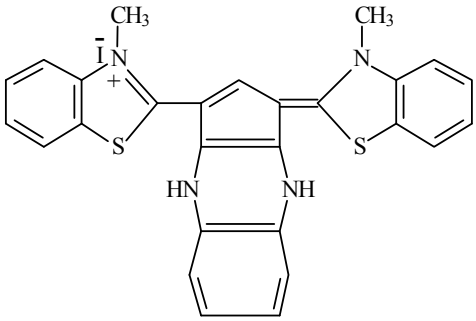
(21)



(22)

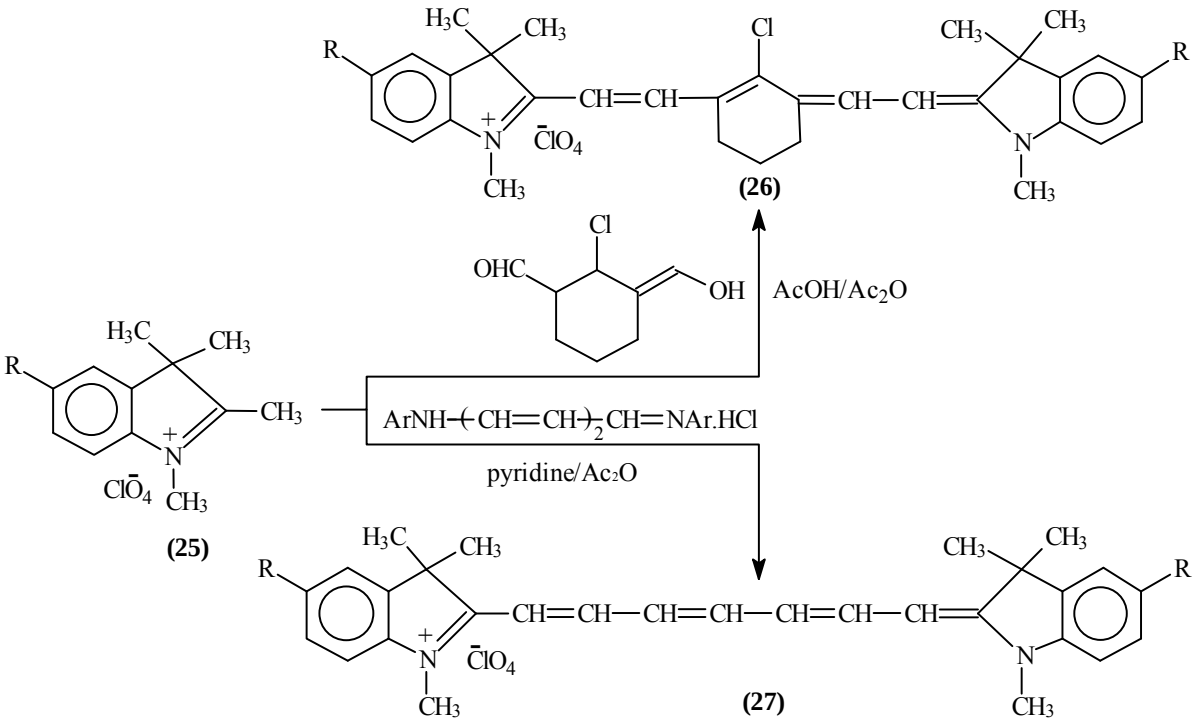


(23)



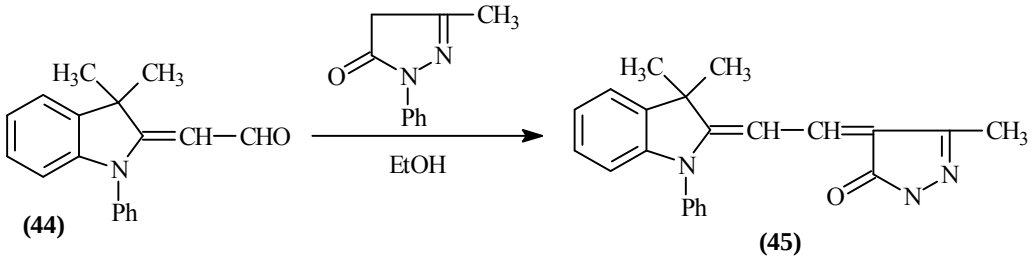
(24)

Scheme 15

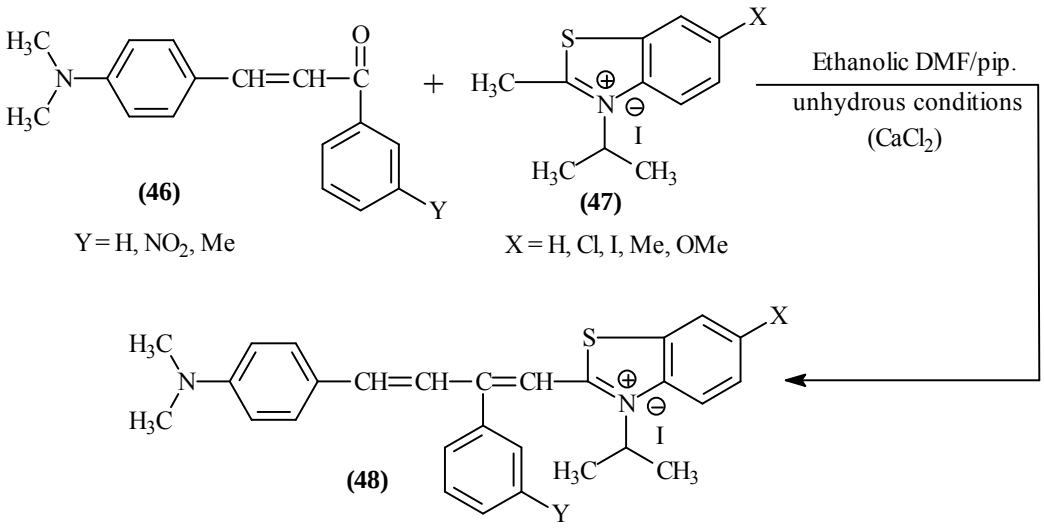


(25) **(26)** **(27)**

Scheme 16



Scheme 17



Scheme 18

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