

Synthesis of Hemicyanine dyes derived from benzothiazole salts and 4, 4'- Bis-dimethylamino phenyl ketone

Dr. Ganga Das

Research scholar,

G D COLLEGE BEGUSARAI DEPARTMENT OF CHEMISTRY.

Abstract

In the present work, it has been proposed to synthesizes hemicyanine dye through preparation of quaternised benzothiazole salts. The preparation of quaternised benzothiazole salts involved into two steps first is preparation of benzothiazoles and Second is Quaternisation. *Synthesis of hemicyanine* derived from quaternised benzothiazole salts and 4, 4 – Bis(dimethylamino) phenyl ketone of five benzothiazole salts. 3-Ethyl-6-iodo-2-(2-4', 4''- bisdimethylamino phenyl ethenyl) benzothiazolium iodide, 6-Chloro-3-ethyl-2-(2-4', 4''- bisdimethyl aminophenylethenyl) benzothiazolium iodide, 3-Ethyl-2-(2-4',4''-bisdimethylaminophenyl ethenyl) benzothiazolium iodide, 3-Ethyl-6-methyl-2-(2-4', 4''- bisdimethyl aminophenylethenyl) benzothiazolium iodide, 3-Ethyl-6-methoxy-2-(2-4, 4''- bisdimethyl aminophenylethenyl) benzothiazolium iodide have been chosen and synthesised in quantitative yield. The use of above mentioned ketones, not only provide a means of weighing in the dye molecule but also furnishes a means to study the role of steric and electronic effect of substitutions in the prime chromophoric methane chain. Keeping in view the multidimensional applications of cyanine and hemicyanine dyes, it was through to synthesise some new hemicyanine dyes by condensing some suitable auxochromic chalcones and benzophenons with quaternised benzothiazolium salts in presence of suitable basic catalyst and study their optical characteristics i.e. U. V. absorption.

Keyword: Cyanine and Hemicyanine dyes, benzothiazolium salts Bis-dimethylamino phenyl ketone and Iodide

Introduction

The first cyanine dye was discovered by Greville Williams but the cyanine dye were not used as a textile dyes because their poor fastness properties. The cyanine and hemicyanine dyes have been used in various purpose. E.g. Photosensitisers, in space photography, as organic photoconductor for electrophotography, as infrared absorbing material for optical recording system in the absorvity and in semiconductor laser. For the present investigation only five quaternised heterocyclic (aromatic) salt (benzothiazole) ten complex auxochromic ketones have been selected for synthesis of dyes. All the five benzothiazole salt base have been synthesized by adopting the method of Jacobson (1886), mills (1992), Beilenson (1936) by procedural alteration suggested by J. C. Banerji (Banerji and Sanyal (1968) and quaternised with ethyl iodide by following the method of Johnson and Adams (1921) with slight modification made by Jha et al (Jha and Banerji 1983, 1985) and Ansari et al (1914, 1995).

Experimentals

In the present work, it has been proposed to synthesize hemicyanine dye through preparation of quaternised benzothiazole salts. The preparation of quaternised benzothiazole salts involved into two steps first is preparation of benzothiazoles and Second is Quaternisation. In the present study all the required chalcones were obtained by a simpler Novel method reported by Jha et al (1987, 1988, 1990, 1995) with some procedural alteration which afforded better yield with high purity. In this developed method Ehrlich's Reagent and substituted acetophenones were dissolved in minimum volume of dry methanol in equimolar quantities and a few pellets of caustic alkali were added. The container was tightly corked and shaken vigorously for about one hour on a magnetic stirrer to get crude coloured chalcone. The product was filtered washed with water and then recrystallised from aqueous ethanol. All prepared chalcones with their physical data are given as follows.

Preparation of benzothiazole:

2-Methyl benzothiazole and its variously 5-substituted derivatives were synthesised by following earlier adopted method (Jacobson 1886; Mills, 1922; Beilenson and Hamer 1936). Alkaline potassium ferricyanide was used for oxidative cyclisation of the thio-acetanilides which afforded crude products. These products were purified by steam distillation (Jacobson, 1886; Jacobson and Ney, 1889; Fries and Engelbertz, 1915; Mills, 1927; Worrall, 1924; Koning, 1928; Beilenson and Hamer, 1936) with some procedural alteration suggested by J.C. Banerji and others (Banerji and Doja, 1949, 1958). In this way five benzothiazole were synthesized which are listed in (table 1).

Hemicyanine dyes derived from benzothiazole salts and 4, 4-bis(dimethylamino) phenyl ketone

Table-1

Sl. No.	X	Name of the hemicyanine dyes	Dyes symbol
1	I	3-Ethyl-6-iodo-2-(2-4', 4"- bisdimethylamino phenyl ethenyl) benzothiazolium iodide.	1(a)
2	Cl	6-Chloro-3-ethyl-2-(2-4', 4"- bisdimethyl amino-phenylethenyl) benzothiazolium iodide	1(b)
3	H	3-Ethyl-2-(2-4',4"-bisdimethylaminophenyl ethenyl) benzothiazolium iodide.	1(c)
4	Me	3-Ethyl-6-methyl-2-(2-4', 4"- bisdimethyl aminophenylethenyl) benzothiazolium iodide.	1(d)
5	OMe	3-Ethyl-6-methoxy-2-(2-4, 4"- bisdimethyl aminophenylethenyl) benzothiazolium iodide	1(e)

Preparation of Hemicyanine dyes

The hemicyanine dyes were synthesized by the thermocatalytic ensation of a 3-ethyl-2-methyl benzothiazolium iodide or its 6-position substituted derivatives with complex auxochromic ketones as suggested by Banerji et al Uha, B.N. and Banerji, J.c. 1983, 1985).

Dyes derived from quaternised benzothiazole salts and 4, 4-Bis(dimethylamino) phenyl ketone
(1) **3-Ethyl-6-iodo-2-(2-4', 4"-bisdimethylaminophenylethenyl) benzothiazolium iodide (1a):**

Preparation:- A proportionate mixture of 3-Ethyl-6-iodo-2-methyl benzothiazolium iodide (0.445g) and 4, 4 Bis (dimethylamino) phenyl ketone (0.268g) mixed solvent (Abs. EtOH; DME 10;1, 20ml) and piperidine (3 drops) were refluxed for 6 hrs in a conical flask, carrying moisture tube at the top of the condenser. After concentration the resultant mixture was left for overnight to crystallize. On recrystallisation of precipitate from methanol the dye was obtained as light yellow sandy crystals.

Analytical data for dye C₂₇ H₂₉ N₃ SI₂ :

Element	Requires in (%)	Found in (%)
Nitrogen	6.17	6.14
Iodine	37.30	32.26

Yield – 23 %, M.P. – 225.8⁰ C

(2) **6 Chloro 3 - ethyl - 2 (2 4' 4'' bisdimethylaminophenyl ethenyl) benzothiazolium iodide (1b):**

Preparation:

6 - Chloro-3- ethyl-2 - methyl benzothiazolium iodide (0.353g) and 4, 4' –bisdimethylamino phenyl ketone (0.268g) were dissolved in minimum volume of absolute ethanol and DMF solvent mixture followed by 3 drops of piperidine. The reaction mixture was refluxed for 6 hrs carrying CaCl-guard tube at the top of condenser. After concentrating the solution it was left overnight to crystallise. The separated dye was recrystallised from methyl alcohol as light brown glazing leaflets.

Analytical data for dye C₂₇ H₂₉ N₃ SCI

Element	Requires in (%)	Found in (%)
Nitrogen	7.12	7.10
Chlorine +Iodine	27.57	27.54

Yield – 23 %, M.P. – 183.4⁰ C

(3) **3-Ethyl- 2- (2 - 4',4''- bis-dimethylaminophenyl ethenyl) benzothiazolium iodide (1c):**

Preparation:- 3-Ethyl -2-Methy-benzothiazolium iodide (0.319g) and Michler's ketone (0.268g) were dissolved in about 15 ml. of absolute and DMF (10:1) mixture followed by the addition of piperidine (3- drops). After fitting moisture tube at the top of the condenser, the mixture was refluxed for 6 hrs in a small conical flask. The resulting mixture was left for overnight after concentration. The separated dye was recrystallised from methanol as tea coloured shining sandy crystals.

Analytical data for dye C₂₇ H₃₀ N₃ SI

Element	Requires in (%)	Found in (%)
Nitrogen	7.57	7.54
Iodine	22.88	22.82

Yield – 22 %, M.P. – 174.5⁰ C

(4) **3 Ethyl-6-methyl- 2- (2 4, 4'' bisdimethylaminophenyl ethenyl) benzothiazoliumiodide(1d):**

Preparation: -In solvent mixture (abs.EtOH: DMF, 10:20m) with basic catalyst piperidine (3 drops), under reflux provided with moisture tube, 2,6 – Dimethyl Denzothiazole ethiodide (0.333g) and 4, 4- Bis (dimethyl

amino) phenyl ketone O.268g) were boiled for 6 hrs. After concentration and cooling afforded dye was recrystallised from methanol as coloured scintillating scales.

Analytical data for dye C₂₈ H₃₂ N₃ SI

Element	Requires in (%)	Found in (%)
Nitrogen	7.38	7.35
Iodine	22.32	22.82

Yield – 27 %, M.P. – 199.5°C

(5) 3-Ethyl 6-methoxy 2-(2-4, 4''-bisdimethylaminophenyl ethenyl) benzothiazoliumiodide(1e):

Preparation:- Mixture containing 3- Ethyl - 6- methoxy benzothiazolium iodide (0.349g) and 4, 4Bis (dimethylamino) phenyl ketone (0.268g) dissolved in ethanol DMF mixture (10:1) in the presence of piperidine (3 - drops) was refluxed for 6 hrs carrying a moisture tube at the top of the condenser. Concentrated and overnight cooled mixture gave the dye which was recrystallised from methanol as brown leaflets.

Analytical data for dye C₂₈ H₃₂ N₃ SI

Element	Requires in (%)	Found in (%)
Nitrogen	7.18	7.15
Iodine	22.71	21.65

Yield – 22 %, M.P. – 204°C

I.R. SPECTRA Ethenyl chain Hemicyanines

Dyes	Absorption Bands (cm ⁻¹)	Assignments
β-(4-Dimethyl amino – phenyl ethenyl) hemicyanine (1a-1e). Dyes no.(1-5)	2970-3030 2410-2450 1440-1680 750-870 500-790	C-H(Str.) (Aromatic) C=N(Str.) (Quarternary -N) C=C (Str.) (Aromatic and Conjugation with C=N, Plane vibration) C-H (Def.) (Aromatic nucleus) C-X (Str.) X=-Cl, -I

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