



ISSN Print: 2394-7500
 ISSN Online: 2394-5869
 Impact Factor: 5.2
 IJAR 2017; 3(1): 920-923
 www.allresearchjournal.com
 Received: 23-11-2016
 Accepted: 27-12-2016

Mobashshir Hassan Khan
 Research Scholar, Department
 of Chemistry, LNMU,
 Darbhanga, Bihar, India

Study of some novel hexamethine quinaldine ascyanine colorants

Mobashshir Hassan Khan

Abstract

The main objective in this paper to study new hexamethine asy-cyanine colorants were synthesized by the reaction of N,N-dimethylaminophenylbutadienyl phenyl ketone, N,N-dimethylaminophenylbutadienyl-4'- bromophenyl ketone and N,N-dimethylamino-phenylbutadienyl-4'-methylphenyl ketone with 2-methyl-N-propyl quinolinium iodide and 6-substituted-2-methyl-N-propyl quinolinium iodides in ethanolic DMF with piperidine catalyst. These colorants were shown to have uniform bathochromic shifts (BS) when compared to analogues with no substituent at β -phenyl nucleus or analogues having dimethine or tetramethine asy-cyanine colorants.

Keywords: hexamethine quinaldine ascyanine colorants

Introduction

There are greatly increasing interests in development of near-infrared absorbing colorants which were used as purpose of optical recording media and bio-fluorescent probes [1, 7]. As Gallium-Arsenic (Ga/As) semiconductor lasers with wave length of (800-830) nm are now being used as a light source for optical information processing systems such as optical disc file equipments and laser beam printing. Also, these colorants are increasingly used as fluorescent tags in DNA sequencing immunoassay. Ascyanine colorants are used for absorptivity, photosensitivity and antimicrobial efficiency.

This paper reports the synthesis & collating of fifteen hexamethine ascyanines with ultraviolet –visible absorption maxima as shown in Scheme - I

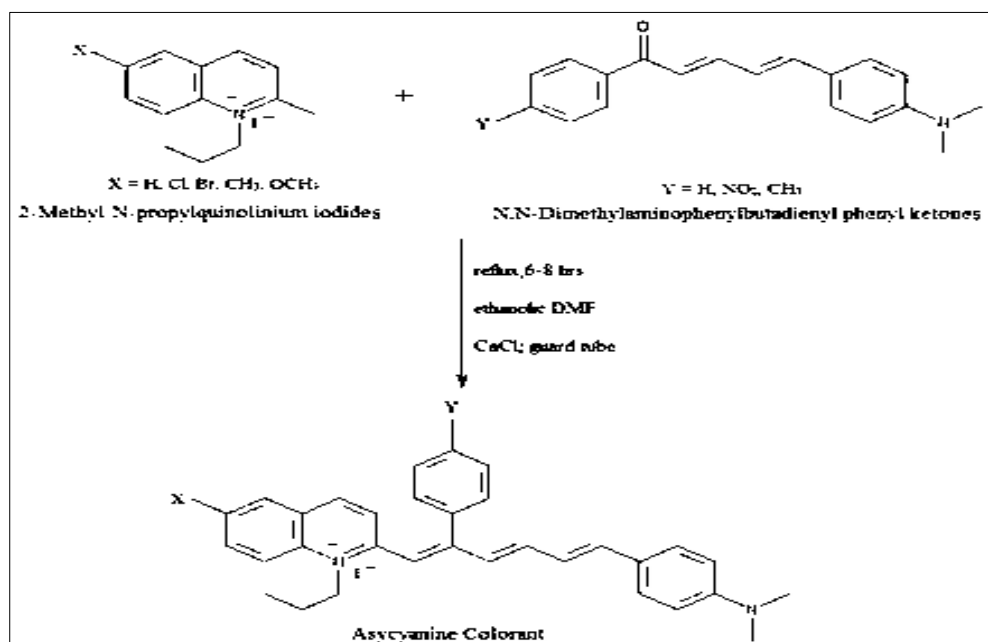


Fig 1: Scheme - I

Corresponding Author:
Mobashshir Hassan Khan
 Research Scholar, Department
 of Chemistry, LNMU,
 Darbhanga, Bihar, India

Materials and Methods

All reagents and solvents were of chemical pure grade and were used without further purification. UV-spectra were determined on a Sistonc 119 UV-spectrophotometer. All melting points are uncorrected and measured in open capillaries in an electrothermal M-21 apparatus IR-spectra (KBr) were recorded Fourier transform spectrophotometer, elemental microanalyzer (H, X) were taken on Perkin Elmer-240 Analyzer.

The auxochromic ketone: For the preparation of auxochromic ketone general methods are adopted with some procedural modifications using N, N-dimethylamino-cinnamaldehyde and acetophenone 4'-nitro/methylacetophenone in pure methanol with pellets of KOH.

4-Dimethylaminophenylbutadienylphenyl ketone: The crude product was re-crystallized from ethanol as dark orange crystals.

m.p. = 136 °C (Lit. yield = 74%; m.p. = 136 °C) Yield = 73%;

4-Dimethylaminophenylbutadienyl-4'-nitrophenyl ketone

The crude product was recrystallised from ethanol as dark red crystalline solid.

Yield = 78%; m.p. = 196°C (Lit. yield = 82%; m.p. = 196 °C)

4-Dimethylaminophenylbutadienyl-4'-methylphenyl ketone

The crude product was recrystallised from ethanol as dark red colored needles.

Yield = 81%; m.p. = 168°C (Lit. yield = 80%; m.p. = 168°C)

The quaternised 2-methyl-N-propylquinolinium iodides:

Five 2-methyl-N-propylquinolinium iodide and 6-substituted-2-methyl-N-propylquinolinium iodide were synthesized and quaternised by earlier methods.

Synthesis of colorants: The condensation to obtain the colorants was carried out by the earlier methods with some modification.

A solution containing the quaternised salt and complex auxochromic ketone in milli molar ratio in ethanolic DMF (25 ml) in the presence of basic catalyst piperidine (2-3 drops) was refluxed for 6-8 hrs under anhydrous conditions using CaCl₂ guard tube. The resulting mixture was concentrated, cooled and left overnight at room temperature. The afforded colorants was recrystallised from methanol. The analytical and UV spectral data of the colorants are given in table 1.

Table 1: Physical parameters

| Colorants | Molecular Formula | X | Y | Colour | Crystal | Yield % | m. p. (°C) |
|-----------------|---|-----------------|-----------------|---------------|--------------|---------|------------|
| C ₁ | C ₃₂ H ₃₃ N ₂ I | H | H | Dark brown | Needles | 70 | 201 |
| C ₂ | C ₃₂ H ₃₂ N ₂ I | Cl | H | Brown | Needles | 74 | 205 |
| C ₃ | C ₃₂ H ₃₂ N ₂ Br | Br | H | Reddish Brown | Needles | 73 | 212 |
| C ₄ | C ₃₃ H ₃₅ N ₂ I | CH ₃ | H | Dark Brown | Flakes | 65 | 218 |
| C ₅ | C ₃₄ H ₃₇ N ₂ O | OEt | H | Brown | Flakes | 76 | 200 |
| C ₆ | C ₃₂ H ₃₂ N ₃ O | H | NO ₂ | Dark Brown | Needles | 72.5 | 190 |
| C ₇ | C ₃₂ H ₃₁ N ₃ O | Cl | NO ₂ | Brown | Needles | 72 | 200 |
| C ₈ | C ₃₂ H ₃₁ N ₃ O | Br | NO ₂ | Violet | Needles | 71 | 196 |
| C ₉ | C ₃₃ H ₃₄ N ₃ O | CH ₃ | NO ₂ | Violet | Needles | 73 | 192 |
| C ₁₀ | C ₃₄ H ₃₆ N ₃ O | OEt | NO ₂ | Dark Brown | Tiny Needles | 74 | 181 |
| C ₁₁ | C ₃₃ H ₃₅ N ₂ I | H | CH ₃ | Violet | Needles | 76 | 216 |
| C ₁₂ | C ₃₃ H ₃₄ N ₂ I | Cl | CH ₃ | Brown | Flakes | 76 | 211 |
| C ₁₃ | C ₃₃ H ₃₄ N ₂ Br | Br | CH ₃ | Violet | Needles | 74 | 201 |
| C ₁₄ | C ₃₄ H ₃₇ N ₂ I | CH ₃ | CH ₃ | Brown | Needles | 72 | 195 |
| C ₁₅ | C ₃₅ H ₃₉ N ₂ O | OEt | CH ₃ | Raddish Brown | Needles | 72 | 193 |

Table 2: Analytical data & Spectral data (UV) of the Colorants

| S. No. | Compounds | %C Cal. (Found) | %H Cal. (Found) | %N Cal. (Found) | %Cl Cal. (Found) | %Br Cal. (Found) | %I Cal. (Found) | Absorption maxima λ (max) (nm) |
|--------|--|-----------------|-----------------|-----------------|------------------|------------------|-----------------|--------------------------------|
| 1 | C ₃₂ H ₃₃ N ₂ I | 67.11 (67.23) | 5.74 (5.74) | 4.87 (4.88) | – | – | 22.10 (2.11) | 570 |
| 2 | C ₃₂ H ₃₂ N ₂ ICl | 6.31 (62.80) | 5.27 (5.22) | 4.61 (4.58) | – | 5.85 (5.81) | 20.93 (20.67) | 580 |
| 3 | C ₃₂ H ₃₂ N ₂ BrI | 58.96 (58.84) | 4.91 (4.79) | 4.30 (4.28) | – | 12.28 (12.22) | 19.50 (19.31) | 580 |
| 4 | C ₃₃ H ₃₅ N ₂ I | 67.55 (67.48) | 5.97 (5.96) | 4.77 (4.74) | – | – | 21.67 (21.43) | 5.83 |
| 5 | C ₃₄ H ₃₇ N ₂ OI | 66.21 (66.33) | 6.00 (5.96) | 4.52 (4.51) | – | – | 20.60 (20.33) | 586 |
| 6 | C ₃₂ H ₃₂ N ₃ O ₂ I | 62.23 (62.08) | 5.18 (5.16) | 6.80 (6.72) | – | – | 20.58 (20.33) | 594 |
| 7 | C ₃₂ H ₃₁ N ₃ O ₂ I | 58.94 (58.42) | 4.73 (4.71) | 6.44 (6.41) | 5.44 (5.42) | – | 19.49 (19.21) | 576 |
| 8 | C ₃₂ H ₃₁ N ₃ O ₂ Br | 55.17 (54.88) | 4.45 (4.51) | 6.03 (6.01) | – | 11.40 (11.38) | 18.24 (18.01) | 587 |
| 9 | C ₃₃ H ₃₄ N ₃ O ₂ I | 6.20 (61.10) | 5.25 (5.21) | 6.49 (6.43) | – | – | 19.62 (19.47) | 580 |
| 10 | C ₃₄ H ₃₆ N ₃ O ₃ I | 61.72 (61.62) | 5.44 (5.41) | 6.35 (6.30) | – | – | 19.21 (19.06) | 586 |
| 11 | C ₃₃ H ₃₅ N ₂ I | 67.57 (67.48) | 5.97 (5.96) | 4.77 (4.74) | – | – | 21.67 (21.43) | 586 |
| 12 | C ₃₃ H ₃₄ N ₂ ICl | 63.81 (63.44) | 5.47 (5.46) | 4.51 (4.49) | 5.70 (5.60) | – | 20.44 (20.12) | 574 |
| 13 | C ₃₃ H ₃₄ N ₂ BrI | 59.54 (59.31) | 5.11 (5.09) | 4.21 (4.20) | – | 12.03 (12.01) | 19.09 (8.84) | 582 |
| 14 | C ₃₄ H ₃₇ N ₂ I | 68.00 (67.62) | 6.16 (6.11) | 4.64 (6.58) | – | – | 20.12 (19.91) | 576 |
| 15 | C ₃₅ H ₃₉ N ₂ OI | 66.66(66.65) | 6.19 (6.10) | 4.42 (4.40) | – | – | 20.15 (19.93) | 580 |

Table 3: Spectral data (I.R.) of the Colorants

| Compounds | Bond Range (Cm-1) | Assignment | | |
|----------------------|---------------------|------------|--|--|
| C _{1,6,11} | 2940-3050 | C-H | Stretching (aromatic) | |
| | 1450-1630 | C=C C=N | Stretching (aromatic) & conjugation with plane Vibration | |
| | 1040-1380 | C-O | Stretching (alkoxy) | |
| | 730-910 | C-H | Bending (aromatic) | |
| | 1320-1360 | C-H | Stretching (aromatic) | |
| | 510-740 | C-X | Stretching | |
| | 1310-1330 | C-N-C | Stretching | |
| | 1630-1660 | C=N | Stretching (conjugated) with aromatic Nucleus | |
| | 2410-2450 | C=N | Quaternary nitrogen | |
| | C _{4,9,14} | 2860-3030 | C-H | Stretching (aromatic) |
| 1430-1630 | | C=C C=N | Stretching (aromatic) & conjugation with plane Vibration | |
| 1055-1390 | | C-O | Stretching (alkoxy) | |
| 710-950 | | C-H | Bending (aromatic) | |
| 1330-1360 | | C-H | Stretching (aromatic) | |
| 510-770 | | C-X | Stretching | |
| C _{5,10,15} | | 2980-3030 | C-H | Stretching (aromatic) |
| | 1420-1630 | C=C C=N | Stretching (aromatic) & conjugation with plane Vibration | |
| | 1040-1330 | C-O | Stretching (alkoxy) | |
| | 710-920 | C-H | Bending (aromatic) | |
| | 1330-1350 | C-H | Stretching (aromatic) | |
| | 500-780 | C-X | Stretching | |
| | 1325-1340 | C-N-C | Stretching | |
| | 1610-1660 | C=N | Stretching (conjugated) with aromatic nucleus | |
| | 2410-2480 | C=N | Quaternary nitrogen | |
| | C _{2,7,12} | 2910-3060 | C-H | Stretching (aromatic) |
| | | 1430-1660 | C=C C=N | Stretching (aromatic) & conjugation with plane Vibration |
| 1020-1380 | | C-O | Stretching (alkoxy) | |
| 710-910 | | C-H | Bending (aromatic) | |
| 1320-1360 | | C-H | Stretching (aromatic) | |
| 520-780 | | C-X | Stretching | |
| 1310-1330 | | C-N-C | Stretching | |
| 1630-1660 | | C=N | Stretching (conjugated) with aromatic nucleus | |
| 2410-2460 | | C=N | Quaternary nitrogen | |
| C _{3,8,13} | | 2910-3030 | C-H | Stretching (aromatic) |
| | 1430-1660 | C=C C=N | Stretching (aromatic) & conjugation with plane Vibration | |
| | 1040-1340 | C-O | Stretching (alkoxy) | |
| | 710-930 | C-H | Bending (aromatic) | |
| | 1330-1360 | C-H | Stretching (aromatic) | |
| | 510-780 | C-X | Stretching | |
| | 1320-1380 | C-N-C | Stretching | |
| | 1640-1680 | C=N | Stretching (conjugated) with aromatic nucleus | |
| | 2420-2455 | C=N | Quaternary nitrogen | |

Results and Discussions

All the colorants are variously substituted-2-methylquinolinium at the position-6-only and are propyl quaternised, besides, β -4'-phenyl nucleus is also substituted. The spectral absorption studies of absorption maxima (λ max) of hexamethine ascyanine colorants lead to significant generalizations.

The β -4'-substituted phenyl butadienyl dyes show uniform bathochromic shifts in the absorption maxima in comparison to their corresponding β -phenyl analogues irrespective of the nature of additional group attached to the β -phenyl nucleus i.e. whether they are electron attracting viz. Cl or electron donating viz. OCH₃ groups.

The bathochromic shifts are more pronounced with β -4'-chlorophenyl nucleus than β -phenyl and β -4'-methoxyphenyl nuclei. Also it has been observed that β -4'-

substituted or unsubstituted phenyl colorants show the similar bathochromic shifts as in styryl colorants.

The substitution in β -phenyl nucleus disturb the benzene ring both by inductive and resonance effects. The change in spectra is more influenced by resonance effect than inductive effects. An electron donating inductive effect (+I) substituent decreases the ionization energy of the substituted benzene while an electron withdrawing inductive effect (-I) substituent increases it. The variation in ionization energy results in bathochromic shifts.

It has been observed that the steric hindrance causes hypsochromic shifts as the much stretched β -phenyl and β -4'-substituted phenyl groups are in close proximity of the main butadienyl chain of the hemicyanine colorants.

Conclusion

In 2-methylquinolinium nucleus, the effect of 6-substituent is small but uniform and systematic for all the hemicyanine colorants. The successive increase in the molecular weight of 6-substituents brings about a successive bathochromic shifts in all the series. The result is in conformity with the 2-methylquinolinium/benzothiazolium colorants the sequenced is in the order as 6-Br > 6-Cl > 6-H in halide series and 6-OCH₃ > 6-CH₃ > 6-H in alkyl and alkoxy series.

References

1. Naryan B, Khan MH, Ali I, Haque MW, Ansari AS. *Oriental J Chem* 2012;28(2):907-911.
2. Ansari AS, Ali I, Haque MW, Khan MH. *Proc. 3rd Bihar Vigyan Congress, G1-11 2010*, 6.
3. Ansari AS, Narayan B, kunwar GK. *J Chinese Chem. Soc* 2006;53:1157-1160.
4. Ernst LA, Gupta RK, Mujumdar RB, Waggoner AS. *Cytometry* 1989;10(3).
5. Matsuoka M. "Infrared Absorption Dyes", Plenum Press, New York 1990.
6. Kagiya M, Yoshida M, Akiyama T, Sugimori A. *Nippon Kagaku Kaishi* 1985, 433.
7. Warning DR, Hallas G Eds. "The Chemistry and Applications of Dyes", Plenum Press, New York 1990.