Synthesis and photophysical properties of pyrrolo\[3,2-c\][1,6] naphthyridin-11(10H)-one derivatives

Raghunath B Toche* & Balasaheb P Pagar

a Dadasaheb Bidkar ASC College, Peth 422 208, Dist. Nashik
b Department of Chemistry, KSW ASC College, Uttamnagar, CIDCO, Nashik 422 008, India
(Affiliated to Savitribai Phule Pune University, Pune 411 007, India)
E-mail: raghunath_toche@rediffmail.com

Received 28 February 2017

Neat reaction of 4,7-dichloro-3-(2-chloroethyl)-2-methylbenzo[h][1,6] naphthyridine-5(6H)-one with aromatic amines gives 2,3-dihydro-9-choro-4-methyl-1H-pyrrolo[3,2-c][1,6] naphthyridin-11(10H)-one in good yields. These new derivatives show high thermal stability with good photophysical properties.

Keywords: 2-Methylbenzo [h] [1,6] naphthyridine-5(6H) -one, 1-aryl-1H-pyrrolo [3,2-c] [1,6] naphthyridin-11(10H)-one, photophysical properties, absorption, emission

Heterocyclic compounds contain aromatic groups or planar or cyclic molecules with several \( \pi \)-bonds that can re-emit light upon light excitation which absorbs in near visible region and emit in the visible region (400-550 nm) are considered to be fluorophores and can be used as the organic light emitting diodes (OLEDs). Fluorescence merely recognized as an ‘odd’ physical or physicochemical phenomenon. However, during the last 50 years, the interest in and application of fluorescent molecules has steadily, sometimes even dramatically, increased and now fluorescent dyes play a central role in many aspects of modern life. In 1927, the British firm Waterlow & Sons used the fluorescent compounds, to prevent forging of bank-notes and other securities. The ability to detect emission at the single molecule level makes fluorescence one of the most sensitive analytical techniques available today. Fluorescence spectroscopy has been widely used in nucleic acid research to study structure and dynamics as well as the kinetics of interactions between DNA and other molecules. Fluorescent brighteners are mainly applied in textile finishing, as additives for laundry detergents, for brightening of pulp and paper and also interest in laser-dye technology. Such molecules absorb in the ultraviolet (UV), especially around 360 nm wavelength, and also fluoresce in the VIS, with typical maxima at 430-440 nm. An increasing number of commercial brighteners are mixtures of two fluorescent compounds which in some cases, give rise to synergetic effects. The chemical or physical base of these phenomena, however, is not yet known. The organic compounds which are used as fluorescent brighteners must have high extinction coefficients, large Stoke shift and quantum yield near to one. Moreover, many heterocycles have been used as organic light emitting diodes (OLED). Any colourless organic compound which has absorption in near visible region and if it fluoresces between 500-700 nm is considered to be good OLED. In 1982 (Ref 6), the research based on molecular modelling started, and chemists were able to predict the fluorescent and electroluminescence properties of the organic compounds. The most important molecular orbital programs were invented such as MOPAC, MM2, PM3, PPP and John A. Pople, one of the inventors of Gaussian70/80 computer programs, received the 1998 Nobel Prize in Chemistry. With these programs, the chemist can calculate the HOMO-LUMO energies of organic compounds theoretically and if the difference between these energies (HOMO-LUMO) is in the range of 2.7−3.0 eV they are considered to be good OLEDs. Fluorescent compounds are widely used as markers in biochemical and nucleic acid technologies. The widely accepted proposals explaining photophysical properties are TICT (twisted intermolecular charge transfer) state model and push-pull mechanism.
of donor-acceptor auxochromes and chromophores. It was also noted that the light emitting diodes must have electron-hole gap between 400 to 700 nm\(^{13}\). The absorption and emission spectra in such cases significantly depend on the type of substituent\(^{14,15}\). The fused heterocyclic compounds are rigid and stable systems possessing high thermal and photochemical stability and are suitable materials for optoelectronic devices. We have reported the synthesis and fluorescent properties of dipyrazolo[3,4-b:3,4-d]pyridines (DPP), pyrazolo[3,4-b]pyrrolo[2,3-d]pyridines (ppp), pyridine-3-carbonitriles, arylbenzo [h] [1,6] naphthyridines and diarylbenzo[h] [1,6] naphthyridines\(^{16-20}\). It was observed that the fluorescent properties of these candidates are dependent upon the nature of donor-acceptor substituents on the C\(_4\)-aryl, which is also the reason for the perpendicular geometry for TICT state. Christoph Hoock et al. reported the synthesis and fluorescent properties of 2,7 - dialkylamino [1,8] naphthyridine derivatives\(^{21}\).

**Results and Discussion**

The 4,67-tridichloro-3-(2-chloroethyl)-2-methylbenzo[h][1,6]naphthyridine\(^{18}\) on refluxing in glacial acetic acid furnished 4,7-dichloro-3-(2-chloroethyl)-2-methylbenzo[h][1,6]naphtydridin-5(6H)-one \(1\) in 93% yield. The compound \(1\) was reacted with primary aromatic amines at 160°C in absence of organic solvent to furnish 2,3-dihydro-9-choro-4-methyl-1-(4-chlorophenyl)-1H-pyrrolo[3,2-c][1,6]napthyridin-11(10H)-one. 2a-l in 49-87% yield (Scheme I).

The structures of compound 2a-l was assigned using spectroscopic and analytical methods. For instance IR of compound 2d showed lactam carbonyl (C=O) stretching at 1668 \text{cm}^{-1} and NH at 3267 \text{cm}^{-1}. The \(^1\)H NMR spectrum of 2d in CDCl\(_3\) showed the resonance singlet at \(\delta\) 2.37 for CH\(_3\) group, two triplets at \(\delta\) 3.22 and 4.25 (\(J = 8.5\) Hz) for CH\(_2\)CHN group, and singlet at \(\delta\) 8.48 (D\(_2\)O exchangeable) was assignable for NH proton. The remaining aromatic protons resonated at expected chemical shifts and had normal splitting patterns. The \(^13\)C NMR spectrum in CDCl\(_3\) showed the frequency corresponding to lactam carbonyl at \(\delta\) 159.22. The mass spectrum showed isotopic peaks at 400 (M+4), 398 (M+2) and 396 (M+) indicating the presence of two chlorine atoms in compound 2d. The elemental analysis is in agreement with molecular formula C\(_{21}\)H\(_{15}\)Cl\(_2\)N\(_3\)O. On the basis of above spectral and analytical data structure was assigned to the compound 2d i.e. 2,3-dihydro-9-choro-4-methyl-1-(4-chlorophenyl)-1H-pyrrolo[3,2-c][1,6]napthyridin-11(10H)-one.

**Thermal properties**

The compounds 2a-l possessing high melting points and high crystallization temperature were studied for their photophysical properties as described below. Thermal analysis of 2a-l by differential scanning calorimetry (DSC) revealed that they are thermally stable compounds up to 300°C.

**Photo physical properties of 1-(4-chlorophenyl) -1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one derivatives**

The empirical calculations of HOMO/LUMO energies of the synthesized compounds 2a-l were done using the MOPAC MP-3 model and are given in Table I. We have studied photo physical properties of 1-aryl-1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-

![Scheme I — Synthesis of 1-aryl-1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one, 2a-l](image-url)
Calculation of the Fluorescence quantum yield

The fluorescence quantum yield ($\Phi_f$) is the ratio of photons absorbed to photons emitted through fluorescence. In other words, the quantum yield gives the probability of the excited state being deactivated by fluorescence rather than by another, non-radiative mechanism. While measurements of the “absolute” quantum yield do require more sophisticated instrumentation\(^2\). It is easier to determine the “relative” quantum yield of the fluorophore by comparing it with a standard known quantum yield. Some of the most common standards used are: Crystal Violet, Fluorescein, quinine sulfate, L-tryptophan, L-tyrosine, \textit{etc}.

The relative quantum yield is generally determined by comparing the wavelength-integrated intensity of the unknown sample with that of the standard. The quantum yield of the unknown sample is calculated using:

$$Q = \frac{I \ OD_R \ n^2}{I_R \ OD \ n_R^2}$$

Where $Q$ is the quantum yield, $I$ is the integrated intensity, $n$ is the refractive index, and $OD$ is the optical density. The subscript $R$ refers to the reference fluorophore of known quantum yield.

The absorption-emission of all synthesized compounds 2a-l was measured by using spectrophotometer RF 3100, and fluorescence quantum yield was calculated by using above equation using quinine sulfate as the reference standard. The results obtained are given in Table II.

It was observed that all the pyrrolo [3, 2-c] [1,6]naphthyridin-11(10H)-one, 2a-l showed fluorescence properties. It is concluded that the compounds 2h, 2i and 2j exhibit remarkable fluorescence characteristics with high quantum yield in comparison with other derivatives. In comparisons compound 2h, 2i and 2j showed absorption, emission maximum equal to (342, 480), (344, 492), (354, 486) nm and quantum yields ($\Phi_f$) 0.30, 0.34, 0.31 respectively. The compound 2k, 2l and 2e showed absorption, emission maximum equal to (392, 421), (331, 430) and (340, 445 nm) and quantum yields ($\Phi_f$) 0.22, 0.23 and 0.24 respectively.

It was observed that the attachment of electron donating group (2h, 2i, 2j) at 4-position on N-phenyl function of pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one derivatives showed enhancement in the

Table I — The molecular electronic properties (HOMO-LUMO energy GAP) of the compounds 2a-l at 25°C

<table>
<thead>
<tr>
<th>Compd</th>
<th>R</th>
<th>Heat of formation (KCal.)</th>
<th>Ionization potential (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>GAP (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>CH$_2$C$_6$H$_5$</td>
<td>105.86</td>
<td>8.845</td>
<td>−8.845</td>
<td>−1.089</td>
<td>7.75</td>
</tr>
<tr>
<td>b</td>
<td>C$_6$H$_5$</td>
<td>74.05</td>
<td>8.776</td>
<td>−8.777</td>
<td>−1.699</td>
<td>7.07</td>
</tr>
<tr>
<td>c</td>
<td>4-FC$_6$H$_4$</td>
<td>134.80</td>
<td>8.945</td>
<td>−8.944</td>
<td>−1.124</td>
<td>7.82</td>
</tr>
<tr>
<td>d</td>
<td>4-ClC$_6$H$_4$</td>
<td>129.63</td>
<td>8.687</td>
<td>−8.687</td>
<td>−0.927</td>
<td>7.76</td>
</tr>
<tr>
<td>e</td>
<td>3-ClC$_6$H$_4$</td>
<td>105.34</td>
<td>8.959</td>
<td>−8.958</td>
<td>−1.168</td>
<td>7.69</td>
</tr>
<tr>
<td>f</td>
<td>2-ClC$_6$H$_4$</td>
<td>121.99</td>
<td>8.873</td>
<td>−8.872</td>
<td>−1.152</td>
<td>7.72</td>
</tr>
<tr>
<td>g</td>
<td>4-BrC$_6$H$_4$</td>
<td>123.54</td>
<td>8.871</td>
<td>−8.871</td>
<td>−1.261</td>
<td>7.61</td>
</tr>
<tr>
<td>h</td>
<td>4-CH$_2$C$_6$H$_4$</td>
<td>64.06</td>
<td>8.856</td>
<td>−8.856</td>
<td>−1.115</td>
<td>7.74</td>
</tr>
<tr>
<td>i</td>
<td>4-OCH$_2$C$_6$H$_4$</td>
<td>142.08</td>
<td>8.981</td>
<td>−8.981</td>
<td>−1.410</td>
<td>7.57</td>
</tr>
<tr>
<td>j</td>
<td>4-NH$_2$C$_6$H$_4$</td>
<td>132.67</td>
<td>8.875</td>
<td>−8.875</td>
<td>−1.175</td>
<td>7.70</td>
</tr>
<tr>
<td>k</td>
<td>4-NO$_2$C$_6$H$_4$</td>
<td>98.23</td>
<td>8.745</td>
<td>−8.745</td>
<td>−0.622</td>
<td>8.12</td>
</tr>
<tr>
<td>l</td>
<td>2-NO$_2$C$_6$H$_4$</td>
<td>128.17</td>
<td>8.999</td>
<td>−8.998</td>
<td>−0.889</td>
<td>8.09</td>
</tr>
</tbody>
</table>

$^a$GAP = $E_{HOMO}$ − $E_{LUMO}$
fluorescence properties as well as higher quantum yield than electron withdrawing group (2k, 2e) at the same position. The comparative absorption and emission spectra of compound 2i and 2c is depicted in Figure 1.

Thermal analysis
The thermal analysis of 2a-l by differential scanning calorimetry (DSC) revealed that these compounds are thermally stable up to 300°C. The absorption spectra of pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-ones 2a-l has been measured and all have \( \lambda_{\text{max}} \) 331-392 nm in DMF. The emission spectra range between 421-492 nm in DMF and the quantum yields \( \Phi_F \) in the range of 0.23-0.34. The fluorescence properties of these compounds depend upon the nature of substituents present on the nitrogen atom of newly annulated pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one derivatives 2a-l. The donor chromophore \( \text{C}_4\text{-OCH}_3 \) showed emission maximum towards red shift (bathochromic shift) and acceptor chromophore \( \text{C}_2\text{-NO}_2 \) showed emission maximum towards blue shift. Whereas in the case of acceptor chromophore \( \text{C}_2\text{-NO}_2 \) and \( \text{C}_4\text{-NO}_2 \) showed the absorption and emission maximum towards blue shift (hypsochromic shift).

Experimental Section
Synthesis of 2,3-dihydro-9-choro-4-methyl-1-aryl-1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one, 2a-l
A mixture of 4,7-dichloro-3-(2-chloroethyl)-2-methylbenzo[h][1,6]naphthyridin-5(6H)-one 1 (0.682 g, 0.02 mmol) and primary aromatic amine (0.05 mmol) was heated to 160°C for 30 min (TLC check). After completion, the reaction mixture was cooled to RT and then methanol (10 mL) was added and resulting solid formed was collected by suction filtration, dried and purified by recrystallization from ethanol to give title compound 2a-l in good yield.

2,3-Dihydro-9-choro-4-methyl-1-benzyl-1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one, 2a: Yellow colored needles. Yield 0.652 g (87%). m.p. 136°C. IR (KBr): 3269, 3236 (NH), 3058, 1674 (C=O), 1650, 1567, 1137, 750 cm^{-1}; \( ^1\text{H NMR} \) (DMSO-\( d_6 \)): \( \delta \) 2.47 (s, 3H, CH\( _3 \)), 3.03 (t, \( J = 8.6 \) Hz, 2H, CH\( _2 \)), 3.87 (t, \( J = 8.6 \) Hz, 2H, CH\( _2 \)N), 5.06 (s, 2H, CH\( _2 \)), 7.10 (t, \( J = 6.7 \) Hz, 2H, ArH), 7.20 (m, 3H, ArH), 7.48 (t, \( J = 7.4 \) Hz, 1H, C\( _2 \)H), 7.78 (d, \( J = 7.4 \) Hz, 1H, C\( _1 \)H), 8.45 (s, 1H, NH, D\( _2 \)O exchangeable), 8.73 (d, \( J = 7.4 \) Hz, 1H, C\( _1 \)H); MS: m/z (%) 377 (M+2, 40), 375 (M+, 90), 298 (70), 284 (60), 270 (50), 167 (70), 91 (50). Anal. Calcd for \( \text{C}_{22}\text{H}_{18}\text{ClN}_3\text{O} \): C, 70.30; H, 4.83; N, 11.18. Found: C, 70.23; H, 4.75; N, 11.24%.

2,3-Dihydro-9-choro-4-methyl-1-phenyl-1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one, 2b: Yellow colored needles. Yield 0.599 g (83%). m.p. 272°C. IR (KBr): 3339 (NH), 3186, 3143, 1676 (C=O lactum), 1249, 734 cm^{-1}; \( ^1\text{H NMR} \) (CDCl\( _3 \)): \( \delta \) 2.70 (s, 3H, CH\( _3 \)), 3.23 (t, \( J = 7.8 \) Hz, 2H, CH\( _2 \)), 4.43 (t, \( J = 7.8 \) Hz, 2H, CH\( _2 \)N), 7.00-7.30 (m, 5H, ArH), 7.46 (t, \( J = 7.2 \) Hz, 1H, C\( _7 \)H), 7.70 (d, \( J = 7.2 \) Hz, 1H, C\( _8 \)H), 8.10 (s, 1H, NH, D\( _2 \)O exchangeable), 8.89 (d, \( J = 7.2 \) Hz, 1H, C\( _6 \)H); MS: m/z (%) 363 (M+2, 30), 361 (M+, 100), 254 (20), 221 (10), 91 (50). Anal. Calcd for \( \text{C}_{21}\text{H}_{16}\text{ClN}_3\text{O} \): C, 69.71; H, 4.46; N, 11.61. Found: C, 69.70; H, 4.49; N, 11.67%.

2,3-Dihydro-9-choro-4-methyl-1-(4-fluorophenyl)-1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one, 2c: Yellow colored prisms. Yield 0.598 g (79%). m.p. 319°C. IR (KBr): 3217 (NH), 3186, 3031, 1672 (C=O), 1564, 1431, 1296, 1247, 756 cm^{-1}; \( ^1\text{H NMR} \) (DMSO-\( d_6 \)): \( \delta \) 2.65 (s, 3H, CH\( _3 \)), 3.06 (t, \( J = 8.6 \) Hz, 2H, CH\( _2 \)N), 7.10 (d, \( J = 7.4 \) Hz, 2H, ArH), 7.20 (m, 3H, ArH), 7.48 (t, \( J = 7.4 \) Hz, 1H, C\( _2 \)H), 7.78 (d, \( J = 7.4 \) Hz, 1H, C\( _1 \)H), 8.45 (s, 1H, NH, D\( _2 \)O exchangeable), 8.73 (d, \( J = 7.4 \) Hz, 1H, C\( _1 \)H); MS: m/z (%) 349 (M+2, 30), 347 (M+, 100), 254 (20), 221 (10), 91 (50). Anal. Calcd for \( \text{C}_{20}\text{H}_{14}\text{ClN}_3\text{O} \): C, 67.51; H, 4.46; N, 11.72. Found: C, 67.49; H, 4.47; N, 11.67%.

Figure 1 — The comparative absorption and emission spectra of compound 2i and 2k
(DMSO-d$_{6}$): δ 2.57 (s, 3H, CH$_{3}$), 3.20 (t, $J = 8.7$ Hz, 2H, CH$_{2}$), 4.22 (t, $J = 8.7$ Hz, 2H, CH$_{2}$N), 6.99-7.16 (m, 4H ArH), 7.18 (t, $J = 7.6$ Hz, 1H, CH$_{3}$), 7.52 (d, $J = 7.6$ Hz, 1H, C$_{H}$), 8.45 (s, 1H, NH, D$_{2}$O exchangeable), 8.67 (d, $J = 7.6$ Hz, 1H, C$_{H}$); $^{13}$C NMR (CDCl$_{3}$): δ 22.56, 25.45, 57.43, 105.01, 119.76, 121.61, 122.22, 124.12, 126.00, 128.25, 129.29, 130.15, 133.24, 145.71, 151.84, 154.16, 156.88, 158.24. Anal. Calcd for C$_{21}$H$_{15}$ClF$_{3}$N$_{4}$(379.82): C, 63.65; H, 3.82; N, 10.60. Found: C, 63.57; H, 3.74; N, 10.53.

2,3-Dihydro-9-choro-4-methyl-1-(4-bromophenyl)-1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one, 2h: Yellow colored prisms. Yield 0.523 g (75%). m.p. 216°C. IR (KBr): 3325 (NH), 3056, 2829 1669 cm$^{-1}$; $^{1}$H NMR (DMSO-d$_{6}$): δ 2.45 (s, 3H, CH$_{3}$), 3.25 (t, $J = 8.3$ Hz, 2H, CH$_{2}$), 4.20 (t, $J = 8.3$ Hz, 2H, CH$_{2}$N), 6.98-7.15 (m, 3H, ArH), 7.22 (t, $J = 7.5$ Hz, 1H, C$_{H}$), 7.26 (s, 1H, ArH), 7.53 (d, $J = 7.5$ Hz, 1H, C$_{H}$), 8.47 (s, 1H, NH, D$_{2}$O exchangeable), 8.73 (d, $J = 7.5$ Hz, 1H, C$_{H}$); $^{13}$C NMR (CDCl$_{3}$): δ 22.44, 25.91, 57.61, 106.07, 118.83, 121.69, 122.51, 124.45, 126.22, 128.62, 129.32, 130.10, 133.48, 139.99, 145.79, 151.85, 154.39, 156.94, 159.26, 167.28; MS: m/z (%) 400 (M+4, 40), 398 (M+2, 60), 396 (M+, 100), 255 (30), 187 (10), 91 (50). Anal. Calcd for C$_{21}$H$_{15}$BrCl$_{3}$N$_{4}$(375.86): C, 70.30; H, 4.83; N, 11.18. Found: C, 70.25; H, 4.70; N, 11.06.

2,3-Dihydro-9-choro-4-methyl-1-(4-tolyl)-1H-pyrrolo[3,2-c][1,6]naphthyridin-11(10H)-one, 2i: Yellow colored prisms. Yield 0.523 g (75%). m.p. 231°C. IR (KBr): 3325 (NH), 3056, 2952, 1668 (C=O), 1519, 1264, 1244, 1174, 767 cm$^{-1}$; $^{1}$H NMR (DMSO-d$_{6}$): δ 2.47 (s, 3H, CH$_{3}$), 3.19 (t, $J = 8.7$ Hz, 2H, CH$_{2}$), 3.40 (s, 3H, OCH$_{3}$), 4.20 (t, $J = 8.7$ Hz, 2H, CH$_{2}$N), 6.70 (d, $J = 8.0$ Hz, 2H, ArH), 7.10 (d., $J = 8.0$ Hz, 2H, ArH), 7.19 (t, $J = 7.6$ Hz, 1H, C$_{H}$), 7.56 (d, $J = 7.6$ Hz, 1H, C$_{H}$), 8.49 (s, 1H, NH, D$_{2}$O exchangeable), 8.70 (d, $J = 7.6$ Hz, 1H, C$_{H}$).
Hz, 1H, C(1)); MS: m/z (%) 393 (M+2, 30), 391 (M, 100), 360 (70), 286 (40), 272 (70) 121 (70), 107 (40). Anal. Calcld for C_{22}H_{33}ClN_2O (391.86): C, 67.43; H, 4.63; N, 10.72. Found: C, 67.33; H, 4.49; N, 10.61%.

2.3-Dihydro-9-choro-4-methyl-1-(4-aminophenyl)-1H-pyrrolo[3,2-c][1,6]naphthyridin-10(1H)-one, 2j: Green colored needles. Yield 0.631 g (84%). m.p. 324°C. IR (KBr): 3234 (NH), 3132, 3026, 1667 (C=O), 1520, 1324, 1245, 1171, 778 cm⁻¹; ¹H NMR (DMSO-d₆): δ 2.42 (s, 3H, CH₃), 3.23 (t, J = 8.7 Hz, 2H, CH₂), 4.18 (t, J = 8.7 Hz, 2H, CH₂N), 4.88 (s, 1H, NH₂), 6.40 (d, J = 7.7 Hz, 2H, ArH), 6.77 (d, J = 7.7 Hz, 2H, ArH), 7.17 (t, J = 7.8 Hz, 1H, C(2)), 7.56 (d, J = 7.8 Hz, 1H, C, 3), 8.53 (d, J = 7.6 Hz, 1H, C, 4), 10.12 (s, 1H, NH, D₂O exchangeable); MS: m/z (%) 378 (M+2, 40), 376 (M+, 100), 360 (40), 284 (70), 270 (30), 254 (20), 106 (30). Anal. Calcld for C_{21}H_{22}ClN₂O (376.85): C, 66.93; H, 4.55; N, 14.87. Found: C, 66.81; H, 4.35; N, 14.67%.

2.4-Dihydro-9-choro-4-methyl-1-(4-nitrophenyl)-1H-pyrrolo[3,2-c][1,6]naphthyridin-10(1H)-one, 2k: Pink colored prisms. Yield 0.522 g (64%). m.p. 313°C. IR (KBr): 3235 (NH), 3142, 3037, 2902, 1668 (C=O), 1537, 1123, 1015, 778 cm⁻¹; ¹H NMR (DMSO-d₆): δ 2.62 (s, 3H, CH₃), 3.26 (t, J = 8.7 Hz, 2H, CH₂), 4.42 (t, J = 8.7 Hz, 2H, CH₂N), 7.10 (d, J = 8.2 Hz, 2H, ArH), 7.23 (t, J = 8.4 Hz, 1H, C, 2), 7.55 (d, J = 8.4 Hz, 1H, C, 3), 8.18 (d, J = 8.2 Hz, 2H, ArH), 8.58 (s, 1H, NH, D₂O exchangeable), 8.71 (d, J = 8.4 Hz, 1H, C, 4).¹³C NMR (CDCl₃): δ 26.09, 29.66, 56.91, 70.20, 117.1, 121.61, 122.83, 124.33, 124.57, 127.09, 130.42, 132.42, 142.33, 151.83, 152.06, 152.43, 158.09, 159.20; MS: m/z (%) 410 (M+2, 40), 408 (M+, 100), 362 (40), 286 (70), 237 (30), 171 (30). Anal. Calcld for C_{22}H_{22}ClN₂O₃ (408.85): C, 61.69; H, 4.19; N, 13.70. Found: C, 61.73; H, 4.25; N, 13.76%.

Conclusion
The 2-chloroethyl-2-methylbenzo[h][1,6]naphthyridine-5(6H)-ones do not show fluorescence properties. The introduction of dihydropyrrole ring shifts absorption and emission to higher wavelengths. It was observed that electron donating substituents e.g. R= OCH₃,C₆H₅, NH,C₆H₅ resulted in red shift, while electron withdrawing substituents e.g. R= NO₂,C₆H₄, ClC₆H₄ resulted in blue shift.

Acknowledgements
Authors thank UGC, New Delhi and BCUD, Savitribai Phule Pune University for financial support, CIF, Department of Chemistry, Savitribai Phule Pune University for spectral analysis and Principal, KTHM College, Nashik for research facilities.

References
1. Waterloò & Sons Ltd., Brit Pat, 22,393 (1927).