Design and synthesis of dichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione to evaluate its optical properties

Pritam Biswas, Debabrata Jana and Chandrakanta Bandyopadhyay*

Department of Chemistry, R. K. Mission Vivekananda Centenary College, Rahara, Kolkata - 700118, West Bengal, India

e-mail: kantachandra@rediffmail.com

Table of contents

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Contents</th>
<th>Page numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Materials and methods</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>General procedure for the synthesis of dichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione (6)</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Analytical data of Compounds 6a-6f</td>
<td>2-4</td>
</tr>
<tr>
<td>4</td>
<td>Copies of $^1$H NMR and $^{13}$C NMR spectra of compound 6a-6f</td>
<td>4-13</td>
</tr>
<tr>
<td>5</td>
<td>Excitation spectra of compounds 6a, 6c, 6d and 6f</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>Absorption spectrum of compound 6f in three different solvents</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>Emission spectra of compound 6f in three different solvents</td>
<td>15</td>
</tr>
</tbody>
</table>
1. **Materials and Methods**

The recorded mps are uncorrected. IR spectra were recorded in KBr on a Shimadzu FTIR spectrophotometer, IR Affinity-1, \(^1\)H NMR / \(^{13}\)C NMR spectra on a bruker 300 MHz / 75 MHz or 400 MHz / 100 MHz spectrometer in CDCl\(_3\) unless stated otherwise, all mass spectra on a Qtof micro YA 263 instrument and elemental analysis on a Perkin Elmer 240c elemental analyzer. Light petroleum refers to the fraction with 60-80 °C. All chemicals used were of commercial grade and were used as such.

2. **General procedure for the synthesis of dichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione 6a-6f:**

![Diagram of synthesis process](image)

A mixture of \(\mathbf{1}\) (0.25 mmol) and \(\mathbf{4}\) (0.25 mmol) was dissolved in acetic acid (5 mL) in a 10 mL round-bottom flask and the resultant solution was heated under reflux in an oil bath for 5 h. The solvent from the reaction mixture was removed under reduced pressure and ice-water (10 g) was added to the concentrate. The deposited solid was filtered out, washed with water, dried in air and crystallized from acetic acid to get white solid 6a-f.

3. **Analytical data of Compounds 6a-6f**

**6a:** Dichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione

![Structural formula of 6a](image)

White solid, yield: (55 mg, 70%); m.p. >290 °C (lit.\(^{17}\) 303 °C); \(\nu_{\text{max}}\) (KBr) 3080, 1670, 1602, 1399 cm\(^{-1}\); \(\delta\)\(_{\text{H}}\) (CDCl\(_3\)) 9.73 (1H, s, H-13), 8.38 (2H, dd, J = 8.0, 1.2 Hz, H-1 and H-11), 7.88-7.84 (2H, m, H-3 and H-9), 7.67 (2H, br d, J = 8.4 Hz, H-4 and H-8), 7.55-7.51 (2H, m, H-2 and H-10); \(\delta\)\(_{\text{C}}\) (DMSO-d\(_6\)) 175.9, 161.5, 155.1, 138.8, 136.6, 126.3, 125.8, 121.1, 118.7, 115.0; HRMS(ESI): Calculated for C\(_{19}\)H\(_9\)NO\(_4\)Na 338.0429, found 338.0437.
**6b: 2-Methyldichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione**

White solid, yield: (55 mg, 67%); m.p. >300 °C; [Found: C, 73.02; H, 3.32; N, 4.21. C_{20}H_{11}NO_{4} requires C, 72.95; H, 3.37; N, 4.25%]; \( \nu_{\text{max}}(\text{KBr}) \) 3090, 1666, 1606, 1463, 1400 cm\(^{-1}\); \( \delta_{H} (\text{CDCl}_{3}) \) 9.70 (1H, s, H-13), 8.35 (1H, dd, \( J = 8.0 \), 1.6 Hz, H-11), 8.14 (1H, br s, H-1), 7.86-7.81 (1H, m, H-9), 7.66-7.63 (2H, m, H-3 and H-8), 7.54 (1H, d, \( J = 8.8 \) Hz, H-4), 7.52-7.48 (1H, m, H-10), 2.51 (3H, s, Me); \( \delta_{C} (\text{CDCl}_{3}) \) 176.2, 176.1, 161.9, 161.8, 155.4, 153.6, 141.2, 137.2, 136.1, 135.7, 127.0, 126.4, 125.6, 121.5, 121.1, 118.5, 118.3, 115.2, 115.0, 20.9; MS: m/z 330 (M+H\(^{+}\)), 352 (M+Na\(^{+}\)).

**6c: 2,10-Dimethyldichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione**

White solid, yield: (50 mg, 58%); m.p. >300 °C; [Found: C, 73.38; H, 3.79; N, 4.04. C_{21}H_{13}NO_{4} requires C, 73.46; H, 3.82; N, 4.08%]; \( \nu_{\text{max}}(\text{KBr}) \) 3040, 1670, 1616, 1599, 1489, 1396 cm\(^{-1}\); \( \delta_{H} (\text{CDCl}_{3}) \) 9.70 (1H, s, H-13), 8.13 (2H, br s, H-1 and H-11), 7.63 (2H, dd, \( J = 8.4 \), 1.6 Hz, H-3 and H-9), 7.53 (2H, d, \( J = 8.4 \) Hz, H-4 and H-8), 2.51 (6H, s, Me-2 and Me-10); \( \delta_{C} (\text{CDCl}_{3}) \) 176.3, 161.8, 153.6, 141.2, 137.2, 135.6, 126.4, 121.2, 118.3, 115.0, 20.9; MS: m/z 344 (M+H\(^{+}\)), 366 (M+Na\(^{+}\)).

**6d: 2-Chloro-10-Methyldichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione**

White solid, yield: (65 mg, 72%); m.p. >300 °C; [Found: C, 65.98; H, 2.73; N, 3.82. C_{21}H_{17}NO_{5} requires C, 66.04; H, 2.77; N, 3.85%]; \( \nu_{\text{max}}(\text{KBr}) \) 3050, 1670, 1597, 1425, 1398 cm\(^{-1}\); \( \delta_{H} (\text{CDCl}_{3}) \) 9.70 (1H, s, H-13), 8.32 (1H, d, \( J = 2.4 \) Hz, H-1), 8.15 (1H, br s, H-11), 7.78 (1H, dd, \( J = 8.8 \), 2.4 Hz, H-3), 7.66 (1H, br d, \( J = 8.4 \) Hz, H-9), 7.62 (1H, d, \( J = 8.8 \) Hz,
H-4), 7.55 (1H, d, J = 8.4 Hz, H-8), 2.53 (3H, s, Me); MS: m/z 364 (M+H⁺), 366 (M+2H⁺), 386 (M+Na⁺), 388 (M+2Na⁺).

6e: 2-Bromodichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione

White solid, yield: (55 mg, 56%); m.p. >280 °C; [Found: C, 57.80; H, 2.02; N, 3.51. C₁₉H₈BrNO₄ requires C, 57.89; H, 2.05; N, 3.55%]; \( \nu_{\text{max}}(\text{KBr}) \) 3030, 1670, 1600, 1552, 1404 cm⁻¹; \( \delta_H \) (CDCl₃) 9.72 (1H, s, H-13), 8.49 (1H, d, J = 2.4 Hz, H-1), 8.38 (1H, dd, J = 8.0, 1.6 Hz, H-11), 7.93 (1H, dd, J = 8.8, 2.4 Hz, H-3), 7.89-7.85 (1H, m, H-9), 7.67 (1H, br d, J = 8.4 Hz, H-8), 7.57 (1H, d, J = 8.8 Hz, H-4), 7.56-7.52 (1H, m, H-10), MS: m/z 394 (M+H⁺), 396 (M+2H⁺), 416 (M+Na⁺), 418 (M+2Na⁺).

6f: 2-Bromo-10-Methyldichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione

White solid, yield: (60 mg, 59%); m.p. >280 °C; [Found: C, 55.79; H, 2.43; N, 3.39. C₂₀H₁₀BrNO₄ requires C, 55.85; H, 2.47; N, 3.43%]; \( \nu_{\text{max}}(\text{KBr}) \) 3065, 1676, 1602, 1552, 1398 cm⁻¹; \( \delta_H \) (CDCl₃) 9.71 (1H, s, H-13), 8.49 (1H, d, J = 2.4 Hz, H-1), 8.15 (1H, d, J = 1.5 Hz, H-11), 7.93 (1H, dd, J = 8.8, 2.4 Hz, H-3), 7.66 (1H, dd, J = 8.4, 1.5 Hz, H-9), 7.57 (1H, d, J = 8.8 Hz, H-4), 7.56 (1H, d, J = 8.4 Hz, H-8), 2.53 (3H, s, Me); MS: m/z 408 (M+H⁺), 410 (M+2H⁺), 430 (M+Na⁺), 432 (M+2Na⁺).

4. Copies of ¹H NMR and ¹³C NMR spectra of compound 6a-6f
5. Excitation spectra of compounds 6a, 6c, 6d and 6f

Fig. A. Excitation spectra of compounds 6a-f in THF

6. Absorption spectra of compound 6f in three different solvents

Fig. B. Absorption spectrum of compound 6f in three different solvents
7. Emission spectra of compound 6f in three different solvents.

**Fig. C.** Normalized emission spectra of compound 6f in three different solvents.