Synthesis of pendant 3-[1,2,3-triazol-2-yl]thieno[2,3-b]pyridines and their application on polyester fibres as fluorescent brighteners

D W Rangnekar & P Y Kamat
Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India
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3-Amino-2-carbethoxy-4, 6-dimethylthieno[2,3-b]pyridine (III) was prepared by the condensation of 2-chloro-3-cyano-4, 6-dimethylpyridine (II) with ethyl thioglycollate and diazotized and coupled with selected arylamines and hetarylamines to give 3-(2-arylamino/hetaryl)azo-2-carbethoxy-4,6-dimethylthieno[2,3-b]pyridines (V). The resulting orthoaminoazo compounds were oxidized with cupric acetate in refluxing DMF in a current of air to get 3-[1,2,3-triazol-2-yl]thieno[2,3-b]pyridine derivatives (VI). The fluorescent properties of pyridine derivatives VI were studied. These compounds when applied as fluorescent brighteners gave moderate whitening effects.

Keywords: Fluorescent brightener, Polyester fibre, 3-[1,2,3-triazol-2-yl]thieno[2,3-b]pyridines

1 Introduction

In the recent years, many heterocyclic structures have been examined for their utility as fluorescent brighteners for polyester fibres. Involvement of 1,2,3-triazole system in many commercial fluorescent brighteners has led us to synthesize a number of heterocyclic derivatives containing 1,2,3-triazole system. In the present study, we report the synthesis of some representative 3-[1,2,3-triazol-2-yl]thieno[2,3-b]pyridines and their application on polyester fibres as fluorescent brighteners.

2 Materials and Methods

The key compound in the synthesis, 3-amino-2-carbethoxy-4,6-dimethylthieno[2,3-b]pyridine (III) was prepared by the condensation of 2-chloro-3-cyano-4, 6-dimethylpyridine (II) with ethyl thioglycollate using anhydrous sodium carbonate in refluxing ethanol. The compound III was diazotized using nitrosyl sulphurous acid and coupled with selected arylamines and hetarylamines, viz. p-chloroaniline (IVa), Tobias acid (2-amino-naphthalene-1-sulphonic acid, IVb) and 1-phenyl-3-methyl-5-aminopyrazole (IVc). The resulting orthoaminoazo compounds, viz. 3-(2-amino-5-chlorophenyl)azo-2-carbethoxy-4,6-dimethylthieno[2,3-b]pyridine (Va), 3-(2-amino-1-naphthyl)azo-2-carbethoxy-4,6-dimethylthieno[2,3-b]pyridine (Vb) and 3-(5-amino-1-phenyl-3-methyl-4-pyrazolyl)azo-2-carbethoxy-4, 6-dimethylthieno[2,3-b]pyridine (Ve) were oxidatively cyclized using cupric acetate in refluxing DMF with a continuous current of air to get the corresponding pendant 3-[1,2,3-triazol-2-yl]-2-carbethoxy-4,6-dimethylthieno[2,3-b]pyridines (VIa-c).
The structures of compounds Va-c and VIa-c were confirmed by their elemental analyses and infrared spectra. The IR spectra of compounds Va-c, recorded in Nujol mull, showed two characteristic peaks of amino group at 3350 and 3450 cm⁻¹ and a peak at 1670-1680 cm⁻¹ corresponding to carbonyl of carbethoxy group. The IR spectra of compounds VIa-c were devoid of the characteristic peaks of amino groups but showed a peak at 1670-1680 cm⁻¹ due to carbonyl of carbethoxy group. The IR spectra of compounds Va-c and VIa-c were further confirmed by their PMR spectra. The PMR spectrum of Va, recorded in DMSO-d₆, exhibited following signals: a multiplet at 0.5-1.0 δ due to three aliphatic protons of methyl of carbethoxy group, a multiplet at 1.5-2.2 δ due to three aliphatic protons of two methyl groups at 4- and 6-positions, a multiplet centered at 3.2 δ due to two aliphatic protons of methylene of carbethoxy group and a multiplet between 6.5-7.2 δ due to six protons of which four are aromatic protons (three of phenyl ring and one of pyridine ring) and two are assigned to amino group. The PMR spectrum of VIa, recorded in DMSO-d₆, showed following signals: a multiplet at 0.5-1.0 δ due to three aliphatic protons of methyl of carbethoxy group, a multiplet at 1.5-2.2 δ due to three aliphatic protons of two methyl groups at 4- and 6-positions, a multiplet at 3.1-3.3 δ due to two aliphatic protons of methylene of carbethoxy group and a multiplet between 6.4 and 7.0 δ due to four aromatic protons (three of phenyl ring and one of pyridine ring).

2.1 Preparation of 3-(2-aminoaryl/hetaryl)azo-2-carbethoxy-4,6-dimethylthieno[2,3-b]pyridines (Va-c)

The compound III (2.5 g, 0.01 mol) was gradually added in 30 min to the previously prepared cold solution of nitrosyl sulphuric acid, obtained on dissolving anhydrous sodium nitrite (0.76 g, 0.011 mol) in conc. sulphuric acid (10 ml), at 10-15°C. After stirring at 10-15°C for further 2 h, the mixture was diluted with glacial acetic acid (100 ml) and the excess of nitrous acid was destroyed with urea (0.2 g). The mixture was then filtered to get a clear diazo solution which was kept at 10°C and used for coupling.

The compound IV (0.01 mol) was dissolved in glacial acetic acid (10 ml) and cooled to 10-15°C. The diazo solution was slowly run into the coupling solution in about 30 min with vigorous stirring at 10-15°C and the mixture was stirred for further 2 h. The mixture was then diluted with crushed ice (about 100 g) and pH of the mixture was adjusted to 5-6 by the careful addition of sodium hydroxide solution (8%). The mixture was further stirred for 2 h at pH 5-6 and temperature 10-15°C. The separated solid was filtered, washed with water, dried and recrystallized from DMF. The characterization data of Va-c are given in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>m.p., °C</th>
<th>Absorption λ max, nm</th>
<th>log ε</th>
<th>Mol. formula</th>
<th>Found (Calcd), %</th>
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<tbody>
<tr>
<td>Va</td>
<td>78</td>
<td>72</td>
<td>400</td>
<td>4.21</td>
<td>C₁₀H₁₇N₂O₂SCl</td>
<td>C 55.36 (55.60) H 4.30 (4.38) N 14.10 (14.41) S 8.40 (8.24)</td>
</tr>
<tr>
<td>Vb</td>
<td>71</td>
<td>153</td>
<td>405</td>
<td>4.12</td>
<td>C₂₂H₂₂N₂O₂S</td>
<td>65.56 (65.35) H 5.20 (4.95) N 13.60 (13.86) S 8.00 (7.92)</td>
</tr>
<tr>
<td>Vc</td>
<td>76</td>
<td>55</td>
<td>425</td>
<td>4.20</td>
<td>C₂₂H₂₃N₂O₂S</td>
<td>60.58 (60.83) H 4.87 (5.07) N 19.10 (19.35) S 7.10 (7.37)</td>
</tr>
</tbody>
</table>

*Crystralization solvent used, DMF.
*Melting points are uncorrected.
Table 2—Characterization data of pendant 3-[1,2,3-triazol-2-yl]thieno[2,3-b]pyridines (VIa-c)

<table>
<thead>
<tr>
<th>Compd</th>
<th>Yield %</th>
<th>m.p., ºC</th>
<th>Absorption ( \lambda_{\text{max}}, ) nm</th>
<th>Emission ( \lambda_{\text{max}}, ) nm</th>
<th>log ( \varepsilon )</th>
<th>Mol. formula</th>
<th>Found (Calcd), %</th>
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<tr>
<td>VIa</td>
<td>62</td>
<td>152</td>
<td>370</td>
<td>454</td>
<td>4.11</td>
<td>C(<em>{15})H(</em>{15})N(_4)O(_2)S(_2)Cl</td>
<td>60.30 (60.69)</td>
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<td></td>
<td>H</td>
<td>5.07 (4.83)</td>
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<td></td>
<td>N</td>
<td>16.28 (16.09)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>S</td>
<td>7.51 (7.36)</td>
</tr>
<tr>
<td>VIb</td>
<td>67</td>
<td>92</td>
<td>344</td>
<td>404</td>
<td>4.03</td>
<td>C(<em>{22})H(</em>{16})N(_4)O(_2)S</td>
<td>55.66 (55.47)</td>
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<td></td>
<td>H</td>
<td>4.01 (4.14)</td>
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<td>N</td>
<td>17.28 (17.03)</td>
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<td></td>
<td></td>
<td></td>
<td>S</td>
<td>7.95 (7.79)</td>
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<tr>
<td>VIc</td>
<td>69</td>
<td>103</td>
<td>340</td>
<td>401</td>
<td>4.01</td>
<td>C(<em>{22})H(</em>{16})N(_6)O(_2)S</td>
<td>63.40 (63.59)</td>
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<td></td>
<td>H</td>
<td>5.16 (5.07)</td>
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<td>N</td>
<td>13.08 (12.90)</td>
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<td></td>
<td></td>
<td></td>
<td>S</td>
<td>7.12 (7.37)</td>
</tr>
</tbody>
</table>

*a* Crystallization solvent used, DMF.

*b* Melting points are uncorrected.

2.2 Preparation of 3-[1,2,3-triazol-2-yl]thieno-[2,3-b]pyridines (VIa-c)

The compound V (0.01 mol) was heated with cupric acetate (1 g, 0.0052 mol) in DMF (10 ml) at 90-95ºC and a continuous current of air was passed through the reaction mixture during heating. The heating was continued until the reaction was complete (2-3 h, monitored by tlc). The reaction mixture was then cooled to room temperature and added to ice cold dil. hydrochloric acid (150 ml, 10%). The separated solid was filtered, washed with water until neutral, dried, and recrystallized from DMF containing a small amount of zinc dust (0.2 g) to get rid of the last traces of unreacted compound V. The characterization data of VIa-c are given in Table 2. The characterization data of VIa-c are given in Table 2.

2.3 Dyeing

The compounds VIa-c were applied on polyester fibres as reported earlier.

3 Results and Discussion

The compounds Va-c were yellow in colour and they were obtained in very good yield (71-78%) (Table 1). The absorption maxima of these compounds, recorded in their DMF solutions, varied from 400 nm to 425 nm and the logarithm of molar extinction coefficient was in the range of 4.12-4.21. The compounds VIa-c were pale yellow in colour and they were obtained in good yield (62-69%) (Table 2). The absorption maxima of these compounds varied from 340 nm to 370 nm and the emission maxima were in the range of 401-454 nm. These compounds thus satisfied the general requirement of fluorescent brighteners which should have absorption maxima in the region close to 350-400 nm and emission in the visible region. The values of logarithm of molar extinction coefficient of these compounds were in the range of 4.01-4.11, indicating their low intensity of absorption.

The compounds VIa-c when applied on polyester fibres as fluorescent brighteners showed whitening effect with greenish-blue fluorescence in the case of compound VIa and violet fluorescence in the case of VIb and VIc. These compounds, on assessment, indicated to be fluorescent brightener of grade one (standard grades of fluorescent brighteners being zero to three).

Acknowledgement

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References