Synthesis of ethyl α-substituted-β-(2-methoxyquinoxalin-6-amino) acrylates and 3-methoxypyrido[3,2-f]quinoxalin-10(7H)-ones and their application on polyester fibres

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6-Amino-2-methoxyquinoxaline (I) obtained from quinoxal-2-one by nitration, chlorination, methoxyla-
tion and reduction was condensed with conjugated en-
ol ethers such as diethyl ethoxymethylene malonic ester (EMME, IIa) and ethyl ethoxymethylene(cyano)acetate (EMCA, IIb) to give ethyl α-substituted-β-(2-methoxyquinoxalin-6-amino) acrylates (III). The cycliza-
tion of III in refluxing dowtherm resulted in the for-
mation of 3-methoxy-9-substituted pyrido[3, 2-f]quinoxalin-10(7H)-ones (IV). The fluorescent prop-
erties of III and IV were studied. When applied on poly-
erster fibres these compounds resulted in poor to
moderate whitening effects.

Keywords: Ethyl α-substituted-β-(2-methoxyquinoxalin-6-amino) acrylate, Fluorescent brightener, 3-Methoxypyrido[3, 2-f]quinoxalin-10(7H)-one, Polyester fibre

A wide variety of heterocyclic compounds have been reported in the recent past as fluorescent compounds. The intrinsic conjugation and rigidity of heterocyclic structures are important in imparting fluorescent properties to heterocyclic derivatives. We have recently reported the synthesis of 6-acetamido-2-substituted quinoxaline derivatives and 6-arylazo-2-methoxyquinoxalines and their application as fluorescent brighteners and disper-
sing dyes on polyester fibres. In the present paper, we report the synthesis of ethyl α-substitut-
ed-β-(2-methoxyquinoxalin-6-amino) acrylates and 3-methoxypyrido[3, 2-f]quinoxalin-10(7H)-
one, their fluorescent properties and application on polyester fibres as fluorescent brighteners.

The application of anthraquinonyl aminoacry-
lates, phthalimido(3-y1/4-y1)aminoacrylates and fused pyrroloquinolinones on polyester fibres has

been reported earlier by us. The introduction of an acrylate substituent in amino group remarkably reduces the basicity of the auxochromic amino group which helps improving the fluorescence intensity of the resulting compounds and moderates dispersibility of these compounds, thus improving their exhaustion from the dye bath when applied on polyester fibres.

6-Amino-2-methoxyquinoxaline (I) prepared by nitration, chlorination, methoxyla-
tion and reduction of quinoxal-2-one was condensed with suitable conjugated enol ethers such as diethyl ethoxymethylene malonic ester (EMME, IIa) and ethyl ethoxymethylene(cyano)acetate (EMCA, IIb) by heating at 180-190°C to give the ethyl α-carbethoxy-β-(2-methoxyquinoxalin-6-amino) acrylate (IIIa) and ethyl α-cyano-β-(2-methoxyquinoxalin-6-amino)acrylate (IIIb) respectively. The amino acrylates IIIa and IIIb were cyclized in refluxing dowtherm to give ethyl 3-methoxypyrido-
[3, 2-f]quinoxalin-10(7H)-one-9-carboxylate (IVa) and 9-cyano-3-methoxypyrido[3, 2-f]quinoxalin-
10(7H)-one (IVb) respectively (Scheme 1).

![Scheme 1—Synthesis of ethyl α-substituted-β-(2-methoxyquinoxalin-6-amino) acrylates and 3-methoxypyrido[3, 2-f]quinoxalin-10(7H)-ones](image-url)
Table 1—Characterization of ethyl α-substituted-β-(2-methoxyquinoxalin-6-amino) acrylates (IIa and IIIb) and 3-methoxy-9-substituted pyrido[3, 2-f]quinoxalin-10(7H)-ones (IVA and IVb)

<table>
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<tr>
<th>Compd</th>
<th>R</th>
<th>Crystallization solvent</th>
<th>Absorption λ&lt;sub&gt;max&lt;/sub&gt;, nm</th>
<th>Emission λ&lt;sub&gt;max&lt;/sub&gt;, nm</th>
<th>Yield %</th>
<th>m.p.°C</th>
<th>Mol. formula</th>
<th>Found (Calcd), %</th>
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<tr>
<td>IIIa</td>
<td>COOC&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Ethyl acetate</td>
<td>319</td>
<td>455</td>
<td>70</td>
<td>127</td>
<td>C&lt;sub&gt;17&lt;/sub&gt;H&lt;sub&gt;19&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>5.3 (5.5)</td>
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<td>11.9 (12.2)</td>
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<td>IIIb</td>
<td>CN</td>
<td>Ethyl acetate</td>
<td>325</td>
<td>450</td>
<td>73</td>
<td>198</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>IVA</td>
<td>COOC&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>DMF</td>
<td>370</td>
<td>409</td>
<td>71</td>
<td>211</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>13.8 (14.1)</td>
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<tr>
<td>IVb</td>
<td>CN</td>
<td>DMF</td>
<td>333</td>
<td>405</td>
<td>75</td>
<td>230</td>
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*Melting points are uncorrected.

The structures of compounds IIIa, IIIb, IVA and IVb were confirmed by their elemental analyses and infrared spectra. The infrared spectra of compounds IIIa and IIIb were recorded in Nujol mull and that of compounds IVA and IVb in KBr disc. The IR spectra of all these compounds showed a broad peak at 3300 cm<sup>-1</sup> corresponding to a secondary amino group and a peak at 1690-1700 cm<sup>-1</sup> (except for IVb) due to the presence of carboxyethoxy group. The IR spectra of compounds IIIb and IVb showed a sharp peak at 2220 cm<sup>-1</sup> corresponding to a cyano group and those of IVA and IVb a peak at 1650 cm<sup>-1</sup> due to the presence of a keto group. The structure of compound IVb was further confirmed by its PMR spectrum. The PMR spectrum, recorded in TFA, exhibited following signals: a multiplet at 3.7 δ due to protons of methoxy group at C<sub>3</sub>, a multiplet between 6.8 and 7.5 δ due to four aromatic protons at C<sub>2</sub>, C<sub>5</sub>, C<sub>6</sub> and C<sub>8</sub> and a D<sub>2</sub>O exchangeable proton at 8.1 δ due to –NH<sub>–</sub> group at N<sub>7</sub>.

Preparation of 3-methoxy-9-substituted pyrido[3, 2-f]quinoxalin-10(7H)-ones (IVA and IVb)

A mixture of compound IIIa or IIIb (0.01 mol) and dowtherm (10 ml) was heated gradually in 2h to reflux and the reflux temperature was maintained until the reaction was complete (9-10h, monitored by tlc). The reaction mixture was cooled and diluted with petroleum ether (b.p., 80-100°C, 40 ml) when a solid separated. The solid was filtered, washed with petroleum ether, dried and recrystallized from DMF. The characterization data of IVA and IVb are given in Table 1.

The compounds IVA and IVb were applied on polyester fibres as reported earlier.<sup>5</sup>

The compounds IIIa and IIIb were pale yellow solids and exhibited daylight blue fluorescence in their DMF solutions. The compounds IVA and IVb were dark brown in colour and exhibited weak violet fluorescence in their DMF solutions. The absorption and emission maxima of IIIa, IIIb, IVA and IVb, recorded in their DMF solutions, are given in Table 1. The emission maxima of compounds IIIa and IIIb were in the 450-455 nm region and those of compounds IVA and IVb in the 405-409 nm region.

The compounds IIIa, IIIb, IVA & IVb were applied on polyester fibres as fluorescent brighteners. The compounds IIIa and IIIb showed moderate whitening effects (grade 1 as compared to standard scale 1-3) and imparted blue fluorescence to polyester fibres, whereas the compounds IVA and IVb showed poor whitening effects (grade...
zero) and imparted weak violet fluorescence. Appropriate substituents in ethyl $\alpha$-substituted-$\beta$-(2-methoxyquinoxalin-6-amino) acrylates may enhance whitening effects on polyester fibres.

**Acknowledgement**

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**References**