POLYMETHINE DYSES FROM ISOMERIC 2-METHYI THIONAPHTHENOTHIAZOLES 

V.* THIENO[3,2-e]BENZOTHIAZOLE DERIVATIVES AS DYSES

Z. I. Moskalenko

A number of quino(2)monomethylidyne-, carbo-, mero-, dimero-, and rhodacyanines (thieno-[3,2-e]benzothiazole derivatives) were synthesized. It is shown that replacement of the vinylene group by a sulfur atom in one of the benzene rings of the naphtho[1,2-d]thiazole residues in the cyanines and merocyanines does not affect the positions of their absorption maxima.

Several cyanine dyes - thieno[3,2-d]benzothiazole derivatives - have been described in the patent literature [2,3]. It seemed of interest to make a more detailed study of the properties of various polymethine dyves with thieno[3,2-e]benzothiazole residues, which are isosteres of the corresponding 2-methyl-naphtho[1,2-d]thiazole derivatives, which have been extensively studied and are finding practical application. For this, we synthesized a number of quino(2)monomethylidyne-, carbo-, mero-, dimero-, and rhodacyanines. Of the known [2,3] methods for the preparation of 2-methylthieno[3,2-e]benzothiazole (IV), we selected that presented in the scheme below (I ~ IV) because of the greater accessibility of the starting compounds. In this case, substantial changes that make it possible to simplify the synthesis were introduced into the individual steps of the synthesis of IV.

\[
\begin{align*}
\text{I} & \xrightarrow{\text{Br}_2} \text{II} & \text{II} & \xrightarrow{\text{CH}_2\text{CSNH}_2, \text{CH}_2\text{OH}} \text{III} & \text{IV} \\
& \xrightarrow{\text{Z}} \text{X-XII}, \text{Xa-XIla} & & \xrightarrow{\text{Z}} \text{XXI, XXIa} & \text{X} = \text{thieno[3,2-e]benzothiazole}, \text{Xa-XIIa, XXIa} & \text{Z} = \text{naphtho[1,2-d]thiazole}
\end{align*}
\]

Compound IV was converted to quaternary salts (V and VI) by the action of methyl and ethyl tosylates. Dyes based on V and VI were obtained by the usual methods adopted for the synthesis of such types of compounds [4-6]. A comparison of the absorption spectra of the carbocyanines (X-XII) and the dimethylidynerocyanines (XXI) of thieno[3,2-e]benzothiazole (Table 1) with the spectra of the corresponding isosteric naphtho[1,2-d]thiazole dyes (Xa-XIIa [7,8] and XIIa [9]) demonstrates that replacement of one vinylene group in the benzene rings of the naphtho[1,2-d]thiazole residues by a sulfur atom has practically no effect on the positions of their absorption maxima. The same dependence is also observed in other classes of dyes that are thieno[3,2-e]benzothiazole derivatives.

The magnitudes of the hypsochromic shifts of merocyanines XXI and XXIa (26.5 and 25.5 nm, respectively), calculated from the absorption maxima of the corresponding symmetrical dyes, demonstrate that the basicities of the thieno[3,2-e]benzothiazole and naphtho[1,2-d]thiazole residues are extremely close.

*See [1] for communication IV.
**TABLE 1. Thieno[3,2-e]benzothiazole Derivative Dyes**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Name</th>
<th>Appearance (from ethanol)*</th>
<th>mp dec.(°C)</th>
<th>Empirical formula</th>
<th>Found, %</th>
<th>Calc., %</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; nm</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII</td>
<td>3,1'-Diethyl-4,5-(3,2-thieno)thiaquin-2'-monomethylidyncyanine iodide</td>
<td>Dark orange needles (800)</td>
<td>268-269</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>5,5</td>
<td>12,4</td>
<td>14,2</td>
<td>504</td>
</tr>
<tr>
<td>VIII</td>
<td>3,1'-Diethyl-4,5-(3,2-thieno)thiaquin-2'-monomethylidyncyanine iodide</td>
<td>Orange needles (1000)</td>
<td>267-268</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>5,4</td>
<td>12,0</td>
<td>12,1</td>
<td>506</td>
</tr>
<tr>
<td>IX</td>
<td>3,1'-Diethyl-4,5-(3,2-thieno)thiaquin-2'-monomethylidyncyanine iodide</td>
<td>Orange needles (700)</td>
<td>262-263</td>
<td>C₃₈H₂₁N₂O₂S₂</td>
<td>5,3</td>
<td>11,7</td>
<td>11,7</td>
<td>513</td>
</tr>
<tr>
<td>X</td>
<td>3,1'-Diethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine iodide</td>
<td>Dark green needles (1000)</td>
<td>249-250</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,6</td>
<td>21,0</td>
<td>21,2</td>
<td>597</td>
</tr>
<tr>
<td>XI</td>
<td>3,1'-Diethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine iodide</td>
<td>Dark blue needles (1000)</td>
<td>231-232</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,7</td>
<td>20,6</td>
<td>20,7</td>
<td>574</td>
</tr>
<tr>
<td>XII</td>
<td>3,1'-Diethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine iodide</td>
<td>Dark green plates (700)</td>
<td>255-256</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,7</td>
<td>20,1</td>
<td>20,2</td>
<td>578</td>
</tr>
<tr>
<td>XIII</td>
<td>3,3',9-Trimethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine p-toluene sulfonate</td>
<td>Green prisms (1000)</td>
<td>231-232</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,4</td>
<td>25,0</td>
<td>25,2</td>
<td>569</td>
</tr>
<tr>
<td>XIV</td>
<td>3,3',9-Trimethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine p-toluene sulfonate</td>
<td>Green needles (400)</td>
<td>263-264</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,3</td>
<td>24,5</td>
<td>24,6</td>
<td>575</td>
</tr>
<tr>
<td>XV</td>
<td>3,3',9-Trimethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine p-toluene sulfonate</td>
<td>Green plates (400)</td>
<td>267-268</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,3</td>
<td>19,8</td>
<td>20,0</td>
<td>598</td>
</tr>
<tr>
<td>XVI</td>
<td>3,3'-Diethyl-4,5'-benz-4,5-(3,2-thieno)thiacarbocyanine iodide</td>
<td>Dark blue needles (1000)</td>
<td>239-240</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,5</td>
<td>15,6</td>
<td>15,7</td>
<td>575</td>
</tr>
<tr>
<td>XVII</td>
<td>3,3'-Diethyl-4,5'-benz-4,5-(3,2-thieno)thiacarbocyanine iodide</td>
<td>Violet plates (500)</td>
<td>242-243</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,6</td>
<td>15,2</td>
<td>15,2</td>
<td>579</td>
</tr>
<tr>
<td>XVIII</td>
<td>3,3'-Diethyl-4,5'-benz-4,5-(3,2-thieno)thiacarbocyanine iodide</td>
<td>Violet needles (1000)</td>
<td>295-296</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>5,0</td>
<td>17,3</td>
<td>17,4</td>
<td>578</td>
</tr>
<tr>
<td>XIX</td>
<td>3,3'-Diethyl-4,5'-benz-4,5-(3,2-thieno)thiacarbocyanine iodide</td>
<td>Red-violet needles (500)</td>
<td>254-255</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>5,0</td>
<td>17,0</td>
<td>17,1</td>
<td>559</td>
</tr>
<tr>
<td>XX</td>
<td>3,3'-Diethyl-4,5'-benz-4,5-(3,2-thieno)thiacarbocyanine iodide</td>
<td>Green prisms (250)</td>
<td>238-239</td>
<td>C₃₈H₂₁N₂S₂</td>
<td>4,8</td>
<td>16,5</td>
<td>16,6</td>
<td>564</td>
</tr>
<tr>
<td>XXI</td>
<td>3-Thioxo-3-ethyl-5-[(1-ethylthieno[3,2-e]benzothiazolylidene)-2-ethylidene]thiazolizin-4-one</td>
<td>Red needles (6000)</td>
<td>299-290</td>
<td>C₃₈H₂₁N₂O₂S₂</td>
<td>6,9</td>
<td>31,6</td>
<td>31,7</td>
<td>542</td>
</tr>
<tr>
<td>XXII</td>
<td>3-Thioxo-3-buty 1-5-[(1-ethylthieno[3,2-e]benzothiazolylidene)-2-ethylidene]thiazolizin-4-one</td>
<td>Red dark prisms (2500)</td>
<td>260-267</td>
<td>C₃₈H₂₁N₂O₂S₂</td>
<td>6,5</td>
<td>29,4</td>
<td>29,5</td>
<td>542</td>
</tr>
<tr>
<td>XXIII</td>
<td>3-Thioxo-3-buty 1-4-oxo-5-(3,2-thieno)thiazolizin-4-one</td>
<td>Green needles (800)</td>
<td>285-286</td>
<td>C₃₈H₂₁N₂O₂S₂</td>
<td>7,4</td>
<td>27,1</td>
<td>27,2</td>
<td>589</td>
</tr>
<tr>
<td>XXIV</td>
<td>3-Thioxo-3-buty 1-4-oxo-5-(3,2-thieno)thiazolizin-4-one</td>
<td>Green needles (800)</td>
<td>292-293</td>
<td>C₃₈H₂₁N₂O₂S₂</td>
<td>5,9</td>
<td>26,2</td>
<td>26,3</td>
<td>623</td>
</tr>
<tr>
<td>XXV</td>
<td>3-Thioxo-3-buty 1-4-oxo-5-(3,2-thieno)thiazolizin-4-one</td>
<td>Green needles (100)</td>
<td>240-241</td>
<td>C₃₈H₂₁N₂O₂S₂</td>
<td>5,6</td>
<td>17,4</td>
<td>17,5</td>
<td>611</td>
</tr>
<tr>
<td>XXVI</td>
<td>3-Thioxo-3-buty 1-4-oxo-5-(3,2-thieno)thiazolizin-4-one</td>
<td>Blue-green needles (200)</td>
<td>196-197</td>
<td>C₃₈H₂₁N₂O₂S₂</td>
<td>5,5</td>
<td>17,3</td>
<td>17,5</td>
<td>629</td>
</tr>
</tbody>
</table>

*The amount of ethanol for the crystallization of the dyes is indicated in parentheses in milliliters per gram.*