

CONDENSED HETEROCYCLES CONTAINING A THIAZOLE RING.

9.\* THIAZOLOTRIAZINOINDOLES

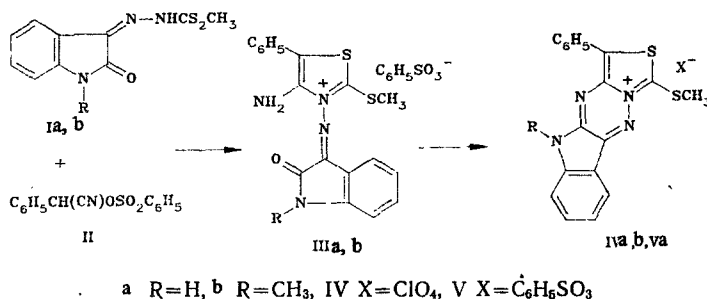
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Condensation of cyanobenzyl benzenesulfonate with isatin N-dithiocarboxyhydrazones has given representatives of a new heterocyclic system, thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium, which may be used for the preparation of polymethine dyes.

Derivatives of condensed heterocyclic systems with a nodal nitrogen atom containing the thiazole and 1,2,4-triazino[5,6-b]indole nuclei have been found to possess valuable properties as physiologically active compounds and dyes [2, 3]. For this reason, it was of interest to obtain derivatives of a new heterocyclic system containing these fragments.

For this purpose, we have examined the reaction of the isatin hydrazones (Ia) and (Ib) with  $\alpha$ -cyanobenzyl benzenesulfonate (II).



The sulfonate (II) is known [4] to react with methyl dithiocarbamate to give the 4-amino-2-methylthiothiazolium salt, and it would therefore be expected that in the present case thiazolium salts (III) would be first formed, which it was then intended to cyclize to give the desired products.

It was in fact found that brief heating of the hydrazone (Ib) with the sulfonate (II) readily afforded the salt (IIIb), the structure of which was confirmed by its IR and UV spectra. For instance, the absorption spectrum of a solution of the compound in acetonitrile shows bands whose maxima (260 and 355 nm) are close to those of the original isatin (Ib) (258 and 373 nm), indicating the presence of a similar moiety in the molecule of the product obtained. The IR spectrum of (IIIb) shows absorption for stretching vibrations of the bonds C=C, C=N, C=O, C-H, and N-H (1500, 1645, 1740, 2820-2920, 3100 cm<sup>-1</sup>), typical isatin hydrazones [5] and 4-aminothiazolium salts [4]. It is noteworthy that the C=N and C=O absorptions in the original hydrazone (Ib) are shifted to lower frequencies (1610 and 1680 cm<sup>-1</sup>) as compared with the analogous absorptions in the salt (IIIb), apparently as a result of intramolecular hydrogen bonding.

Further investigations showed that on heating the aminothiazole (IIIb) with trifluoroacetic or toluene-p-sulfonic acid a colored product was obtained, which from its elemental analysis and IR and PMR spectra (see the Experimental section) was assigned the structure (IVb). For example, the IR spectrum of the thiazolotriazinoindole (IVb) contained no absorption for C=O and N-H stretching, present in that of the original salt (IIIb), only C=N stretching vibrations (1615 cm<sup>-1</sup>) being seen.

\*For Communication 8, see [1].

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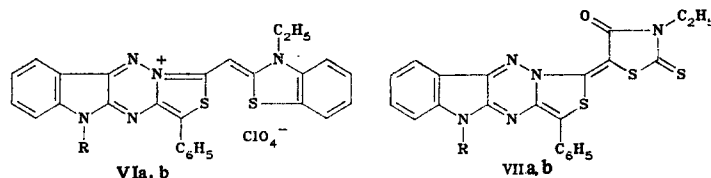
TABLE 1. Properties of Compounds Obtained

Compound	Mp, * deg C	$\lambda_{max}$ , nm (log e)	Found, %			Empirical formula	Calculated, %			Yield, %
			Cl	N	S		Cl	N	S	
IIIb	204—207	355	—	10,9	17,7	C <sub>25</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> S <sub>3</sub>	—	10,4	17,9	85
IV a	269—270	540 (3,49)	8,0	—	14,5	C <sub>18</sub> H <sub>13</sub> ClN <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	7,9	—	14,3	87
IV b	263—264	554 (3,60)	7,5	—	13,8	C <sub>19</sub> H <sub>15</sub> ClN <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	7,7	—	13,8	69
Va	264—265	540 (3,51)	—	10,9	18,7	C <sub>24</sub> H <sub>18</sub> N <sub>4</sub> O <sub>3</sub> S <sub>3</sub>	—	11,1	18,9	71
VIa	>310	617 (3,87)	5,9	12,0	—	C <sub>27</sub> H <sub>20</sub> ClN <sub>5</sub> O <sub>4</sub> S <sub>2</sub>	6,1	12,1	—	85
VIb	305—306	625 (3,87)	5,8	—	10,8	C <sub>28</sub> H <sub>22</sub> ClN <sub>5</sub> O <sub>4</sub> S <sub>2</sub>	5,9	—	10,9	63
VIIa	312—313	690 (3,72)	—	15,2	20,4	C <sub>22</sub> H <sub>15</sub> N <sub>5</sub> OS <sub>3</sub>	—	15,2	20,8	73
VIIb	309—310	695 (3,63)	—	15,1	20,1	C <sub>23</sub> H <sub>17</sub> N <sub>5</sub> OS <sub>3</sub>	—	14,8	20,2	94

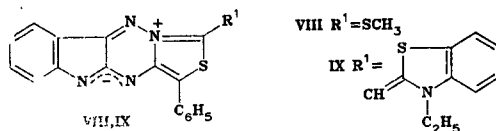
\*Compound (IVa) was crystallized from acetic acid, (IVb) from a mixture of acetic and formic acids (10:1), (Va) from a mixture of acetic acid and ethyl acetate (2:1), (VIa) from nitromethane with the addition of 57% perchloric acid, (VIb) from a mixture of acetic acid and nitromethane (3:1), (VIIa) from DMF, and (VIIb) was washed with DMF.

Reaction of the dithiocarboxyhydrazone (Ia) with the benzenesulfonate (II) gave initially the 4-aminothiazolium compound, which then under the reaction conditions cyclized directly to the thiazolotriazinoindole, the structure of which was also confirmed by its elemental analysis and its IR and PMR spectra.

The thiazolotriazinoindolium compounds obtained, like the quaternary salts of 2-methylthiothiazole, react readily with the nucleophilic intermediates used in the synthesis of polymethine dyes. For instance, 2-methyl-3-ethylbenzthiazolium to toluenesulfonate gives the monomethinecyanines (VIa, b), and 3-ethylrhodanine gives the zeromethinecyanine dyes (VIIa, b).



It is interesting that on adding triethylamine to a solution of the 5-unsubstituted thiazolotriazinoindolium salt (IVa) or to the monomethinecyanine (VIa) obtained from this compound, there is a bathochromic shift of the long-wavelength absorption band by 115 and 63 nm (3321 and 1463 cm<sup>-1</sup>), respectively, indicating [6] the formation of mesoionic compounds with structures (VIII) and (IX).



Acidification of solutions of (VIII) and (IX) results in the restoration of the saltlike thiazolotriazinoindolium derivatives.

#### EXPERIMENTAL

Electronic spectra were obtained on an SF-8 spectrophotometer in acetonitrile; IR spectra, on a UR-10 spectrophotometer in KBr disks; and PMR spectra, on a BS-467 radiospectrometer (60 MHz) in trifluoroacetic acid, internal standard HMDS.

The properties of the compounds obtained are given in Table 1.

4-Amino-3-(1-methyl-2-oxo-2,3-dihydro-3-indolylidene)amino-2-methylthio-5-phenylthiazolium Benzenesulfonate (IIIb). A mixture of 2.65 g (10 mmoles) of the hydrazone (Ib) [7] and

3 g (11 mmoles) of  $\alpha$ -cyanobenzyl benzenesulfonate (II) was heated for 10 min at 100°C. The melt was triturated with acetonitrile, and the solid filtered off and washed with acetonitrile. Yield 4.56 g.

5-Methyl-1-methylthio-5-phenyl-5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (IVb). A mixture of 0.54 g (1 mmole) of the benzenesulfonate (IIIb) and 0.17 g (1 mmole) of toluene-p-sulfonic acid was heated for 20 min at 90°C. The melt was triturated with acetic acid, and a solution of 0.13 g (1 mmole) of sodium perchlorate in 2 ml of acetic acid added. The solid which separated was filtered off, and crystallized to give 0.32 g. PMR spectrum: 2.60 (s, 3H); 3.32 (s, 3H); 6.8-7.8 ppm (m, 9H).

1-Methylthio-3-phenyl-5H-thiazolo[3',4':2,3]-1,2,4-triazono[5,6-b]indolium Benzene-sulfonate (Va). A mixture of 2.54 g (10 mmoles) of the hydrazone (Ia) and 3 g (11 mmoles) of  $\alpha$ -cyanobenzyl benzenesulfonate (II) was heated for 20 min at 100°C. The melt was triturated with acetone, and the solid filtered off and recrystallized. Yield 0.34 g.

1-Methylthio-3-phenyl-5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (IVa). To a solution of 0.45 g (1 mmole) of the benzenesulfonate (Va) in 15 ml of acetic acid was added a solution of 0.13 g (1 mmole) of sodium perchlorate in 2 ml of acetic acid. The product was filtered off and recrystallized, yield 0.39 g.

3-Phenyl-1-(3-ethylbenzthiazolin-2-ylidene)methyl-5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (VIa). A mixture of 0.45 g (1 mmole) of the perchlorate (IVa) and 0.35 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium tosylate in 50 ml of alcohol was brought to the boil, and 0.1 g (1 mmole) of triethylamine was added. The dye was filtered off and crystallized. Yield 0.36 g.

5-Methyl-1-(3-ethylbenzthiazolin-2-ylidene)methyl-3-phenyl-5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium perchlorate (VIb) was obtained as for (VIa), from the perchlorate (IVb).

2-Thioxo-3-ethyl-5-[3-phenyl-5H-1(1H)thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolyli-dene]thiazolidin-4-one (VIIa). A mixture of 0.45 g of the perchlorate (IVa) and 0.16 g (1 mmole) of 3-ethylrhodamine in 10 ml of alcohol was brought to the boil, and 0.15 g (1.5 mmoles) of triethylamine added. The dye was filtered off and crystallized. Yield 0.34 g.

2-Thioxo-3-ethyl-5-[5-methyl-5H-1(1H)-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolyli-dene]thiazolidin-4-one (VIIb) was obtained as for (VIIa), from (IVb).

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