

POLYMETHINE DYE DERIVATIVES OF PYRAZOLO[4,5-d]THIAZOLE

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Quino(2)monomethine-, carbo-, mero-, dimero-, and rhodacyanines, as well as styryl dyes containing 4-methyl-6-phenyl- and 4,6-diphenylpyrazolo[4,5-d]thiazoles groupings are prepared. Study of the colors of the synthesized dyes, showed that dyes containing a pyrazolo[4,5-d] moiety to be considerably more deeply colored, than the corresponding benzothiazole derivatives.

It was previously [1] shown that treatment of 2,4-dimethyl-6-phenyl- and 2-methyl-4,6-diphenylpyrazolo[4,5-d]thiazoles with alkylating agents gives quaternary salts of potential interest as starting materials for preparing various polymethine dyes.

To synthesize a symmetrical carbocyanine derived from 4-methyl-6-phenylpyrazolo[4,5-d]thiazole, an attempt was made to condense a quaternary salt of the base with ethyl orthoformate in pyridine [2] or nitrobenzene (see e.g. [3]). However, it did not prove possible to obtain that particular dye in that way. It was synthesized by reacting the ethylperchlorate of 2,4-dimethyl-6-phenylpyrazolo[4,5-d]thiazole with ethyl orthoformate in acetic anhydride, followed by condensation of the resultant ethylperchlorate of the 2- β -ethoxyvinyl derivative (cf. [4]) with a quaternary salt of the 2-methyl substitution product of the same base in acetic anhydride, in the presence of triethylamine. Heating 2- β -acetanilovinylbenzothiazole ethiodide with a quaternary salt of 2,4-dimethyl-6-phenyl- or 2-methyl-4,6-diphenylpyrazolo[4,5-d]thiazole in pyridine-acetic anhydride, or acetic anhydride plus triethylamine (cf. [5]) gave unsymmetrical carbocyanines. The corresponding meso-methyl and -ethyl substituted dyes were obtained by condensing ethylethyl sulfates of the base with chloroethylates of 2- β -chloropropenyl- and -butenylbenzothiazoles in dry ethanol in the presence of triethylamine (cf. [6]).

To synthesize a pyrazolothiazolodimethymerocyanine, a quaternary salt of 2,4-dimethyl-6-phenyl- or 2-methyl-4,6-diphenylpyrazolo[4,5-d]thiazole was condensed with 3-ethyl-5-acetanilinomethylenerhodanine in dry ethanol in the presence of triethylamine (cf. [7]). It was shown that when the 5-chloromethylene derivative was used in place of the 3-ethyl-5-acetanilinomethylenerhodanine (cf. [8]), the yield of dye was considerably raised. In addition a convenient method of preparing dimethinemerocyanines was reaction of the ethylperchlorate of β -ethoxyvinyl derivatives of the bases with 3-ethylrhodanine, which was effected in acetic anhydride in the presence of triethylamine.

When 2- β -anilovinyl-4-methyl-6-phenylpyrazolo[4,5-d]thiazole methiodide was condensed with 3-ethyl-5-ethylidene- or 5- α -ethoxyethylidenerhodanine in acetic anhydride plus triethylamine (cf.

[9]), tetramethinemerocyanines were obtained.

Rhodacyanine and dimerocyanine syntheses were effected by heating a quaternary salt of an α -dimethylmercapto derivative of pyrazolo[4,5-d]thiazolodimethinemerocyanine with the ethylethyl sulfate of 2-methyl-4,5-diphenylthiazole or 3-butylrhodanine in pyridine (cf., e.g., [10]), respectively.

Styryl and quino(2)monomethinecyanine dyes were obtained respectively by reacting a quaternary salt of 2,4-dimethyl-6-phenylpyrazolo[4,5-d]thiazole with p-dimethylaminobenzaldehyde or 2-ethylmercaptoquinoline ethiodide, in acetic anhydride or dry ethanol and triethylamine.

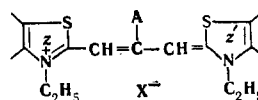
Tables 1 and 2 give the positions of the absorption maxima of carbocyanine and merocyanine dyes, and for comparison those of the corresponding benzothiazole derivative dyes (measurements were made with a SF-2M spectrophotometer).

The data of Tables 1 and 2 show that on passing from a dye with a benzothiazole group, to the corresponding pyrazolo[4,5-d]thiazolo compound the absorption maximum is displaced towards the longwave region of the spectrum. The hypsochromic shift of the absorption maximum on introducing a methyl or ethyl group at the meso position in the polymethine chain of pyrazolo[4,5-d]thiazolothiacarbocyanine, is of the same order, as for thiocarbocyanine (Table 1).

The hypsochromic shift of the absorption maxima of 4-methyl-6-phenylpyrazolo[4,5-d]thiazolodimethinemerocyanine, as calculated from the absorption maxima of the corresponding oxanine and carbocyanine dyes, (Table 2), is almost the same as the shift for the corresponding dye containing a benzothiazole group, indicating that the basicities of the 4-methyl-6-phenylpyrazolo[4,5-d]thiazole and benzothiazole groups are about the same. Actually the value of A (the concentration of hydrochloric acid, mole/l, bringing about shift, in $1 \cdot 10^{-5}$ M solution in 57% ethanol, to the diacid salt) found for the diethylate of the symmetrical carbocyanine, a derivative of 4-methyl-6-phenylpyrazolo[4,5-d]thiazole, was 2.2 compared with 2.8 for the corresponding dye containing a benzothiazole group instead.

EXPERIMENTAL

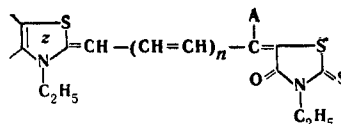
2- β -anilovinyl-4-methyl-6-phenylpyrazolo[4,5-d]thiazole ethiodide (I). 1 g (0.003 mole) 2,4-dimethyl-6-phenylpyrazolo[4,5-d]thiazole ethiodide, 0.4 g (0.003 mole) orthoformic ester, and 0.24 g (0.003 mole) aniline were heated together for 1 hr at 100° C. The resultant crystalline mass was heated with 1 ml dry acetone, the solid filtered off, and washed with

Table 1. Absorption Maxima in Ethanol (in $m\mu$) of Dyes

| Z | A | | |
|--|----------|-----------------|-------------------------------|
| | H | CH ₃ | C ₂ H ₅ |
| 4-Methyl-6-phenylpyrazolo[4, 5-d]thiazole* | 558 | — | — |
| Benzothiazole | 558 [11] | 543 [12] | 547 [13] |
| 4-Methyl-6-phenylpyrazolo[4, 5-d]thiazole | 569 | 556 | 561 |
| 4, 6-Diphenylpyrazolo-[4, 5-d]thiazole | 573 | 558 | — |

*Z') 4-methyl-6-phenylpyrazolo[4, 5-d]thiazole, in the other examples it was benzothiazole.

Table 2. Absorption Maxima and Hypsochromic Shifts of the Dyes, in Ethanol



| Z | n | A | λ_{max} , $m\mu$ | $\Delta\lambda$, $m\mu$ |
|---|---|--------------------------------|--------------------------|--------------------------|
| 4-Methyl-6-phenylpyrazolo[4, 5-d]thiazole | 0 | H | 538 | 25,0 |
| Benzothiazole | 0 | H | 524 [14] | 26 [14] |
| 4, 6-Diphenylpyrazolo[4, 5-d]thiazole | 0 | H | 538 | — |
| 4-Methyl-6-phenylpyrazolo[4, 5-d]thiazole | 1 | H | 624 | — |
| 4-Methyl-6-phenylpyrazolo[4, 5-d]thiazole | 1 | OC ₂ H ₅ | 623 | — |
| Benzothiazole | 1 | H | 607 [15] | — |

Table 3. Pyrazolo[4,5-d]thiazole Derivative Dyes

| Dye number | Name | Appearance | Mp (decomp), °C | Formula | N, % | | Yield, % |
|------------|---|----------------------|-----------------|--|-------------------------|------------|--------------|
| | | | | | Found | Calculated | |
| II* | 1', 3'-Diethyl-4-methyl-6-phenylpyrazolo[4,5-d]thiazolo-2'-quinocyanine iodide | Red needles | 245—246 | C ₂₃ H ₂₃ IN ₄ S | 10.06 | 10.37 | 5.6 |
| III | 3, 3'-Diethyl-4, 4'-dimethyl-6, 6'-diphenylpyrazolo[4,5-d], 5, 1'-d, 4', 5, 1'-d, 5, 1'-d]-thiazolocarbo-cyanine perchlorate | Green needles | 300—301 | C ₂₃ H ₂₉ ClN ₆ O ₄ S ₂ | 10.07 13.45 13.47 | 13.44 | 32.2 |
| IV | 3, 3'-Diethyl-4-methyl-6-phenylpyrazolo[4,5,1'-d]thiazolothiacarbo-cyanine iodide | Green needles | 235—236 | C ₂₃ H ₂₃ IN ₄ S ₂ | 9.63 9.65 | 9.79 | 22.8 |
| V | 3, 3'-Diethyl-4, 8-dimethyl-6-phenylpyrazolo[4,5,1'-d]thiazolothiacarbo-cyanine iodide | Bluish-green needles | 250—252 | C ₂₆ H ₂₇ IN ₄ S ₂ | 9.17 9.18 | 9.48 | 33.9 |
| VI | 3, 3', 8-Triethyl-4-methyl-6-phenylpyrazolo[4,5-d]thiazolothiacarbo-cyanine iodide | Dark-green prisms | 218—219 | C ₂₇ H ₂₉ IN ₄ S ₂ | 9.10 9.11 | 9.33 | 26.7 |
| VII | 3, 3'-Diethyl-4, 6-diphenylpyrazolo[4,5,1'-d]thiazolothiacarbo-cyanine iodide | Green needles | 208—209 | C ₃₀ H ₂₇ IN ₄ S ₂ | 8.58 8.65 | 8.82 | 10.8 |
| VIII | 3, 3'-Diethyl-4, 6-diphenyl-8-methylpyrazolo[4,5,1'-d]thiazolothiacarbo-cyanine iodide | Violet needles | 174—175 | C ₃₁ H ₂₉ IN ₄ S ₂ | 8.60 8.55 | 8.64 | 14.6 |
| IX | 3-Ethyl-5-{3'-ethyl-4'-methyl-6'-phenylpyrazolo[4,5,1'-d]thiazolothiazolylidene-2'-ethylidene}thiazolidine-2'-thione-4'-one | Reddish-brown plates | 219—220 | C ₂₀ H ₂₀ N ₄ OS ₃ | 12.82 13.03 | 13.08 | 41.2 48.8 |
| X | 3-Ethyl-5-{3'-ethyl-4', 6'-diphenylpyrazolo[4,5,1'-d]thiazolylidene-2'-ethylidene}thiazolidine-2'-thione-4'-one | Green needles | 245—247 | C ₂₈ H ₂₂ N ₄ OS ₃ | 11.33 11.37 | 11.43 | 17.0 |
| XI | 3-Ethyl-5-{3'-ethyl-4'-methyl-6'-phenylpyrazolo[4,5,1'-d]thiazolylidene-2'-butenylidene}thiazolidine-2'-thione-4'-one | Green needles | 204—205 | C ₂₂ H ₂₂ N ₄ OS ₃ | 12.25 12.28 | 12.31 | 26.1 |
| XII | 3-Ethyl-5-{3'-ethyl-4'-methyl-6'-phenylpyrazolo[4,5,1'-d]thiazolylidene-2'-α-ethoxybutenylidene}thiazolidine-2'-thione-4'-one | Green plates | 162—163 | C ₂₄ H ₂₆ N ₄ O ₂ S ₃ | 11.12 11.17 | 11.22 | 24.0 |
| XIII* | 3, 3'-Diethyl-4-keto-4', 5'-diphenyl-5-{3''-ethyl-4''-methyl-6''-phenylpyrazolo[4,5,1'-d]thiazolylidene-2''-ethylidene}thiazolothiazolocarbo-cyanine iodide | Brown needles | 243—244 | C ₃₈ H ₃₆ IN ₅ S ₃ | 8.89 9.00 | 9.07 | 47.3 |
| XIV* | 2-(3'-Butylthiazolidine-2'-thione-4'-one-5'-ylidene)-3-ethyl-5-3''-ethyl-4''-methyl-6''-phenylpyrazolo[4,5,1'-d]thiazolylidene-2''-ethylidene}thiazolid-4-one | Green needles | 255—256 | C ₂₇ H ₂₈ O ₂ N ₅ S ₄ | 11.85 11.88 | 11.99 | 53.9 |
| XV* | 2-p-Dimethylaminostyryl-4-methyl-6-phenylpyrazolo[4,5,1'-d]thiazole ethiodide | Violet needles | 215—216 | C ₂₃ H ₂₁ IN ₄ S | 10.64 10.66 | 10.93 | 52.8 |

*λ_{max} (in EtOH) II: 495 mμ, XIII 606 mμ, XIV 585 mμ, XV 526 mμ.

acetone. Yield 0.47 g (33.5%), mp 207°–208° C, yellow needles (ex EtOH) mp 208°–209° C. Found: N 11.48%. 11.27%. Calculated for $C_{21}H_{21}IN_4S$: N 11.48%.

Dyes (Table 3). The monomethinecyanine II was synthesized by heating together at 125° C for 15 min 0.001 mole 2,4-dimethyl-6-phenylpyrazolo[4,5-d]-thiazole and 0.001 mole 2,4-dimethyl-6-phenylpyrazolo[4,5-d]thiazole and 0.001 mole diethyl sulfate, and then condensing the resultant salt with 0.001 mole 2-ethylmercaptoquinoline ethiodide in 3 ml EtOH, in the presence of 0.002 mole Et_3N . The symmetrical carbocyanine III was prepared by heating together at 140° C, for 1 hr, 0.001 mole of the base ethylperchlorate, 0.002 mole orthoformic ester, and 1 ml Ac_2O , then condensing the resultant product, without first isolating it, with quaternary salt of the same base in 5 ml Ac_2O in the presence of 0.004 mole Et_3N , by heating the compounds together for 5 min on a boiling water-bath. The unsymmetrical carbocyanines IV–VIII were synthesized by heating together for 5–10 min, at 100° C, 0.001 mole 2,4-dimethyl-6-phenyl- or 2-methyl-4,6-diphenylpyrazolo[4,5-d]thiazole ethylethylsulfate, 0.001 mole 2- β -anilino vinylbenzothiazole ethyltosylate or 2- β -chloropropenyl- and -butenylbenzothiazole methochloride respectively, in 3 ml EtOH or 2 ml EtOH or 2 ml Ac_2O and 0.002 mole Et_3N . Dimethinemerocyanines IX–X were obtained by condensing 0.001 mole base quaternary salt with 0.001 mole 5-chloromethyl-3-ethylrhodanine or 0.001 mole ethylperchlorate of the β -ethoxyvinyl derivatives of the bases with 0.001 mole 3-ethylrhodanine in 2 ml Ac_2O and 0.006 mole Et_3N by heating together on a boiling water-bath for 5–10 min. Tetramethinemerocyanines XI–XII were synthesized by reacting 0.005 mole I with 0.005 mole 3-ethyl-5-ethylidene- or 5- α -ethoxyethylidenerhodanine in 3 ml Ac_2O with 0.002 mole Et_3N , at 100° C. Rhodacyanine XIII and dimerocyanine XIV were prepared by heating 0.001 mole dimethinemerocyanine IX with 0.002 mole Me_2SO_4 for 15 min at 125° C, then condensing the resultant product with 0.001 mole ethylsulfate of 2-methyl-4,5-diphenylthiazole or of 3-butylrhodanine respectively, in 3 ml pyridine, for 20–45 min at 130° C. The styryl dye XV was synthe-

sized by heating 0.0007 mole 2,4-dimethyl-6-phenylpyrazolo[4,5-d]thiazole with 0.0007 mole p-dimethylaminobenzaldehyde in 2 ml Ac_2O for 40 min at 120° C.

All the dyes were purified by recrystallizing from EtOH.

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