INVESTIGATIONS IN THE FIELD OF SYNTHETIC DYES

LXVI. The Synthesis of Quinomerocyanine Dyes Containing a Methoxy or Hydroxy Group in the Quinoline Nucleus*

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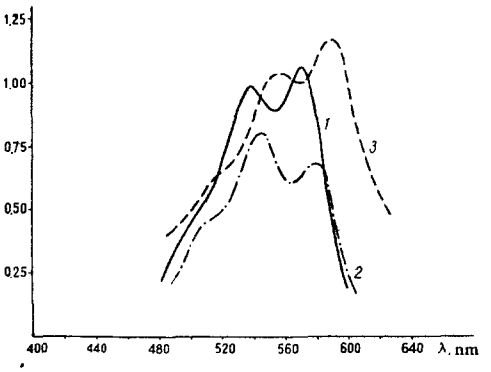
Quinomerocyanines forming derivatives of rhodanine, oxazolone, and pyrazolone have been synthesized. The presence of a methoxy or a hydroxy group in the quinoline nucleus and in the p-position of a phenyl radical attached to the nitrogen leads to a bathochromic displacement of the absorption maximum as compared with the unsubstituted dye.

In order to study the influence of hydroxy and methoxy groups on the optical properties of the dimethinequinomerocyanines, we have synthesized the appropriate dyes by condensing 6-methoxy-1-p-methoxyphenylquinaldinium perchlorate [1], 6-hydroxy-1-p-hydroxyphenyllepidinium iodide [2], 6-methoxy-1-p-methoxyphenyllepidinium iodide [2], and 1-p-methoxyphenylquinaldinium perchlorate [3] with 5-acetanilidomethylenerhodanine, 5-acetanilidomethylene-3-ethylrhodanine, 5-ethoxymethylene-3-phenylrhodanine, 4-ethoxymethylene-3-methyl-1-phenyl-5-pyrazolone, and 4-ethoxymethylene-2-phenyl-5-oxazalone [4–8]. For comparison, a number of dyes were also obtained from 1-phenyllepidinium perchlorate [9] and 6-methyl-1-p-tolyllepidinium perchlorate [3] (see table).

The absorption curve of 3-ethyl-5-(1'-ethyldihydroquinol-2'-ylideneethylidene)-4-oxo-2-thiazolidinethione [5] in ethanol has two maxima, the longer-wave one being the more intense (see figure). The replacement of the ethyl radical on the nitrogen atom by a phenyl radical weakens the basicity of the quinoline nucleus and the short-wave maximum becomes stronger. The introduction of a methoxy group into the p-position of the phenyl radical on the nitrogen atom somewhat weakens its electron-accepting properties, which causes a small bathochromic displacement of the absorption maximum of the dye (I, II, III). The introduction of a methoxy group into position 6 of the quinoline nucleus and into the p-position of the phenyl radical on the nitrogen atom (VI, VII, VIII) increases the basicity of the quinoline nucleus to such an extent that this is shown not only in a bathochromic displacement but in the fact that the long-wave maximum becomes the main one (see figure). For the dyes XI-XIII and XVI-XVIII, the introduction of a hydroxy or a methoxy group into the quinoline nucleus and into the p-position of the phenyl radical attached to the nitrogen atom causes a considerable bathochromic displacement as compared with the unsubstituted dye.



Absorption spectra of ethanolic solutions of the merocyanine dyes: 1) 3-ethyl-5-(1'-ethyldihydroquinol-2'-ylideneethylidine)-4-oxothiazolidine-2-thione; 2) 3-ethyl-4-oxo-5-(1'-phenyldihydroquinol-2'-ylideneethylidene)-thiazolidine-2-thione; 3) 3-ethyl-5-(6'-methoxy-1'-p-methoxyphenyldihydroquinol-2'-ylideneethylidene)-4-oxo-2-thiazolidinethione.

In the case of the oxazolone and pyrazolone dyes, the introduction of a substituent into the quinoline nucleus is not accompanied by a change in the nature of the curve, which is fairly symmetrical in ethanol for these dyes. The presence of a hydroxy or a methoxy group in the quinoline nucleus and in the phenyl radical attached to the nitrogen heteroatom causes a bathochromic shift of the absorption band in all cases (dyes IV, V, IX, X, XIV, XV, XIX).

EXPERIMENTAL

Quinomerocyanine dyes (see table). Equimolecular amounts of the quaternary salt, the intermediate from the rhodanine, oxazolone, or pyrazolone compound, and triethylamine (or piperidine) were boiled in anhydrous ethanol or pyridine (1–2 minutes for the reaction with ethoxymethylenephenyloxazolone, 10–30 minutes for the reaction with acetanilidomethyleneethylrhodanine, and ethoxymethylenephenylrhodanine, and 1–1 1/2 hr for the reaction with acetanilidomethylenerhodanine). The crystals that deposited were washed with ethanol and ether.

In some cases, a trimethinecyanine dye was formed, and this precipitated together with the merocyanine. The trimethinecyanine dye was removed by boiling the precipitate with ethanol.

*For part LXV, see [12].

Table 1

Properties of the Dimethylquinomerocyanines Synthesized

Compound	Name	Mp (decomp.), °C (solvent for crystallization)	λ_{max}, nm		Empirical formula	N, %		Yield, %
			of the dye synthesized	of the corresponding dye without a substituent in the quinoline nucleus		found	calculated	
1	2	3	4	5	6	7	8	9
I	5-(1'-p-Methoxyphenyldihydroquinol-2'-ylideneethylidene)-4-oxo-2-thiazolidinethione	273–275 (pyridine and ethanol)	548	542, 575[11]	$C_{21}H_{16}N_2O_2S_2$	6.80; 6.86	7.13	46
II	3-Ethyl-5-(1'-p-methoxyphenyldihydroquinol-2'-ylideneethylidene)-4-oxo-2-thiazolidinethione	248–250 (n-butanol)	546 578	544, 578[10]	$C_{23}H_{20}N_2O_2S_2$	6.62; 6.90	6.66	62
III	5-(1'-p-Methoxyphenyldihydroquinol-2'-ylideneethylidene)-4-oxo-3-phenyl-2-thiazolidinethione	252–254 (n-butanol)	548 581	545, 580[10]	$C_{27}H_{20}N_2O_2S_2$	6.23; 6.28	5.98	78
IV	4-(1'-p-Methoxyphenyldihydroquinol-2'-ylideneethylidene)-3-methyl-1-phenyl-5-pyrazolone	222–224 (n-butanol)	530	525	$C_{28}H_{23}N_3O_2$	9.42; 9.47	9.69	44
V	4(1'-p-Methoxyphenyldihydroquinol-2'-ylideneethylidene)-2-phenyl-5-oxazolone	239–241 (n-butanol)	552	549	$C_{27}H_{20}N_2O_3$	6.78; 6.92	6.66	74
VI	5-(6'-Methoxy-1'-p-methoxyphenyldihydroquinol-2'-ylideneethylidene)-4-oxo-2-thiazolidinethione	265–266 (pyridine and ethanol)	586	542, 575	$C_{22}H_{18}N_2O_3S_2$	6.37; 6.41	6.63	50
VII	3-Ethyl-5-(6'-methoxy-1'-p-methoxyphenyldihydroquinol-2'-ylideneethylidene)-4-oxo-2-thiazolidinethione	232–233 (acetic acid)	557 590	544, 578	$C_{24}H_{22}N_2O_3S_2$	6.13; 6.37	6.21	57
VIII	5-(6'-Methoxy-1'-p-methoxyphenyldihydroquinol-2'- ylideneethylidene)-4-oxo-3-phenyl-2-thiazolidinethione	302–304 (acetic acid)	556 590	545, 580	$C_{28}H_{22}N_2O_3S_2$	5.77; 5.83	5.62	80
IX	4-(6'-Methoxy-1'-p-methoxyphenyldihydroquinol-2'-ylideneethylidene)-1-phenyl-5-pyrazolone	270–271 (n-butanol)	536	525	$C_{29}H_{25}N_3O_3$	9,30; 9.35	9.06	59
X	4-(6'-Methoxy-1'-p-methoxyphenyldihydroquinol-2'-ylideneethylidene)-2-phenyl-5-oxazolone	220–222 (n-butanol)	564	549	$C_{28}H_{22}N_2O_4$	6.44; 6.50	6.22	84
XI	5-(6'-Methoxy-1'-p-methoxyphenyldihydroquinol-4'-ylideneethylidene)-4-oxo-2-thiazolidinethione	280–282 (pyridine and ethanol)	582 622	570, 610	$C_{22}H_{18}N_2O_3S_2$	6.49; 6.80	6.63	74

Table 1 (Cont'd)

1	2	3	4	5	6	7	8	9
XII	3-Ethyl-5-(6'-methoxy-1'-p-methoxyphenyldihydroquinol-4'-ylideneethylidene)-4-oxo-2-thiazolidinethione	238–239 (n-butanol)	588 630	577, 617	$C_{24}H_{22}N_2O_3S_2$	6.27; 6.02	6.21	78
XIII	5-(6'-Methoxy-1'-p-methoxyphenyldihydroquino-4'-ylideneethylidene)-4-oxo-3-phenyl-2-thiazolidinethione	249–250 (pyridine and ethanol)	590 632	579, 619	$C_{28}H_{22}N_2O_3S_2$	5.49; 5.54	5.62	80
XIV	4-(6'-Methoxy-1'-p-methoxyphenyldihydroquino-4'-ylideneethylidene)-3-phenyl-5-pyrazolone	247–248 (n-butanol)	581	578	$C_{29}H_{25}N_3O_3$	9.24; 9.32	9.06	57
XV	4-(6'-Methoxy-1'-p-methoxyphenyldihydroquinol-4'-ylideneethylidene)-2-phenyl-5-oxazolone	227–228 (n-butanol)	590 632	580, 622	$C_{28}H_{22}N_2O_4$	6.44; 6.30	6.22	67
XVI	5-(6'-Hydroxy-1'-p-hydroxyphenyldihydroquinol-4'-ylideneethylidene)-4-oxo-2-thiazolidinethione	250–252 (n-butanol)	582 628	570, 610	$C_{20}H_{14}N_2O_3S_2$	7.38; 7.31	7.10	40
XVII	3-Ethyl-5-(6-Hydroxy-1'-p-hydroxyphenyldihydroquinol-4'-ylideneethylidene)-4-oxo-2-thiazolidinethione	285–287 (n-butanol)	590 631	577, 617	$C_{22}H_{18}N_2O_3S_2$	6.67; 6.47	6.63	42
XVIII	5-(6'-Hydroxy-1'-p-hydroxyphenyldihydroquinol-4'-ylideneethylidene)-4-oxo-3-phenyl-2-thiazolidinethione	289–290 (pyridine and ethanol)	590 632	589, 619	$C_{26}H_{18}N_2O_3S_2$	6.20; 5.84	5.91	78
XIX	4-(6'-Hydroxy-1'-p-hydroxyphenyldihydroquinol-4'-ylideneethylidene)-3-methyl-1-phenyl-5-pyrazolone	283–284 (pyridine and ethanol)	581	578	$C_{27}H_{21}N_3O_3$	9.80; 9.75	9.63	54
XX	4-Oxo-5-(1'-phenyldihydroquinol-4'-ylideneethylidene)-2-thiazolidinethione	285–287 (pyridine and ethanol)	570 610	—	$C_{20}H_{14}N_2OS_2$	7.43; 7.51	7.73	95
XXI	3-Ethyl-4-oxo-5-(1'-phenyldihydroquinol-4'-ylideneethylidene)-2-thiazolidinethione	249–251 (acetic acid)	577 617	—	$C_{22}H_{18}N_2OS_2$	7.26; 7.33	7.07	71
XXII	4-Oxo-3-phenyl-5-(1'-phenyldihydroquinol-4'-ylideneethylidene)-2-thiazolidinethione	295–297 (pyridine and ethanol)	579 619	—	$C_{26}H_{18}N_2OS_2$	6.32; 6.48	6.38	98
XXIII	5-(6'-Methyl-1'-p-tolyldihydroquinol-4'-ylideneethylidene)-4-oxo-2-thiazolidinethione	290–291 (pyridine and ethanol)	571	570, 610	$C_{22}H_{18}N_2OS_2$	7.16; 6.97	7.17	70
XXIV	3-Ethyl-5-(6'-methyl-1'-p-tolyldihydroquinol-4'-ylideneethylidene)-2-thiazolidinethione	273–275 (acetic acid)	582 623	577, 617	$C_{24}H_{22}N_2OS_2$	6.75; 6.78	6.69	69
XXV	5-(6'-Methyl-1'-p-tolyldihydroquinol-4'-ylideneethylidene)-4-oxo-3-phenyl-2-thiazolidinethione	279–281 (acetic acid)	580 625	579, 619	$C_{28}H_{22}N_2OS_2$	5.97; 5.97	6.00	95

REFERENCES

1. G. T. Pilyugin and B. M. Gutsulyak, ZhOKh, 31, 623, 1961; G. T. Pilyugin and N. A. Tsvetkova, ZhOKh, 34, 3341, 1964.

2. G. T. Pilyugin and B. M. Gutsulyak, ZhOKh, 32, 1051, 1962.

3. G. T. Pilyugin and B. M. Gutsulyak, ZhOKh, 30, 1299, 1960.

4. Z. P. Sytnik, I. I. Levkoev, and M. V. Deichmeister, ZhOKh, 21, 768, 1951.

5. M. V. Deichmeister, Z. P. Sytnik, and E. B. Lifshits, ZhOKh, 22, 166, 1952.

6. Chien-Pen Zo and W. J. Croxall, J. Am. Chem. Soc., 76, 4166, 1954.

7. P. B. Tripathy and M. K. Rout, J. Sci. and Ind. Res., B20, 4, 177, 1961.

8. A. H. Cook, G. Harris, and G. Shaw, J. Chem. Soc., 1435, 1949.

9. G. T. Pilyugin and B. M. Gutsulyak, ZhOKh, 29, 3076, 1959.

10. S. V. Lepikhova and G. T. Pilyugin, KhGS [Chemistry of Heterocyclic Compounds], 275, 1965.

11. G. T. Pilyugin and S. V. Lepikhova, ZhOKh, 35, 647, 1965.

12. S. V. Lepikhova and G. T. Pilyugin, ZhOrKh, 1, 1129, 1965.

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