Chemistry of Heterocyclic Compounds, Vol. 32, No. 8, 1996

PYRYLOCYANINES.

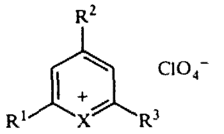
35.* SQUARYLIUM DYES BASED ON tert-BUTYL-SUBSTITUTED PYRYLIUM AND THIOPYRYLIUM SALTS

V. V. Kurdyukov, M. A. Kudinova, and A. I. Tolmachev

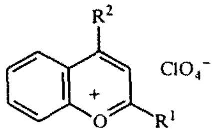
Squarylium dyes based on isomeric di(tert-butyl)methyl-substituted pyrylium, thiopyrylium, and benzopyrylium salts have been synthesized. The dye containing 4,6-di(tert-butyl)pyrylium residues was converted to its analog with methylpyridinium residues. The PMR and electronic absorption spectra of the dyes obtained were investigated. It was established that deepening of the color from dicarbocyanines to squaraines is characteristic only of dyes containing heterocyclic residues with high or medium electron-donor capacity. For dyes containing heterocyclic residues with low electron-donor capacity the opposite pattern is observed.

As a result of their selective and intensive absorption, as well as their high photochemical stability [2], squarylium dyes have proved promising for use as photoreceptors in solar batteries, photoconductors for xerography [3], and also in the development of the recording media of optical memory devices [2, 4-6]. Therefore, the dyes of this group, especially those that absorb in the near-IR region, where diode lasers widely used for optical recording emit, are evoking ever increasing interest. Despite this, the dependence of the spectral properties of squarylium dyes on their chemical structure has received little investigation. It has been shown that as we go from a squarylium dye containing 2,6-di(tert-butyl)pyrylium residues to its sulfur-, selenium-, and tellurium-containing analogs, a deepening of the color is observed [7], as in the usual polymethine dyes with an unsubstituted chromophore. On the basis of the spectral properties of squarylium dyes, derivatives of 2-quinoline and benzthiazole, which have colors 18 and 12 nm, respectively, deeper than the corresponding analogous dicarbocyanine derivatives, in [8] it is concluded that closing of the squarylium ring of the dicarbocyanine chromophore leads to a deepening of the color. This conclusion is repeated in the review [6]. The fact that the color deepens by 9 nm in the transition from indodicarbocyanine to the corresponding squarylium dye, cited in [8], is not commented upon.

From the standpoint of the systematic investigations that we are conducting in the field of pyrylocyanines, in this work we undertook to produce squarylium dyes that are pyrylium and thiopyrylium derivatives and to investigate some of their chemical conversions and spectral properties. In the synthesis of the indicated compounds we used pyrylium salts of the Ia,b, IIa,b [9], III [10], IV, and V [11] types. The dyes (VIa,b, VIIa,b, and VIII-X) were synthesized by condensation of these salts



I, II a, b; III



IV, V

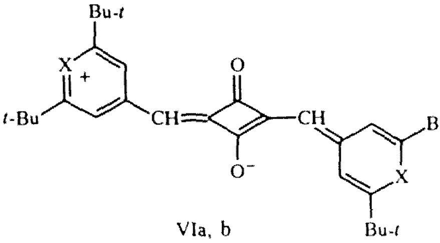
I $R^1 = R^3 =$ Bu-*t*, $R^2 =$ Me; II $R^1 = R^2 =$ Bu-*t*, $R^3 =$ Me; III $R^1 =$ Ph, $R^2 =$ Bu-*t*, $R^3 =$ Me;
Ia, IIa, III X = O; Ib, IIb X = S; IV $R^1 =$ Bu-*t*, $R^2 =$ Me; V $R^1 =$ Me, $R^2 =$ Bu-*t*

---

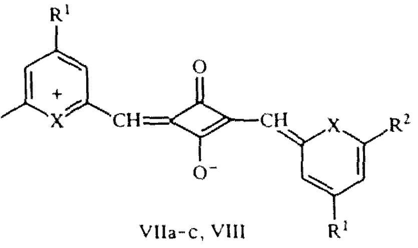
*For communication 34, see [1].

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev, 253660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1038-1044, August, 1996. Original article submitted May 8, 1996.

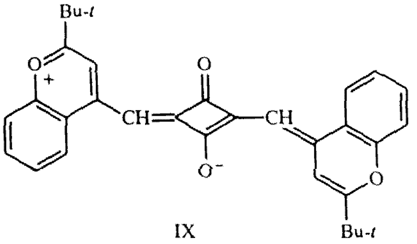
with squaric acid, performed according to the well-known procedure [12] in a mixture of toluene and n-butanol in the presence of quinoline. On the example of the squarylium dye that is a derivative of α-pyrylium VIIa it was shown that, just as in the case of the usual pyrylocyanines [9] in the interaction with methylamine recyclization of the corresponding squarylium dyes to pyridinium derivatives (VIIc) can also occur. Of the compounds VIa,b described earlier [7], the thiopyrylium derivative VIb possesses the optimum characteristics for use in optical memory devices; therefore it is repeatedly encountered in the patent literature (see [4] and the references cited in it). Even before the salts IIa,b were described, the dyes VIIa [13] and VIIb [13, 14] were mentioned in the patents.



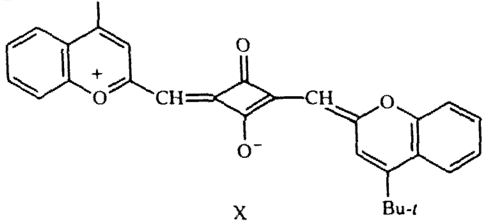
VIa, b



VIIa-c, VIII



IX

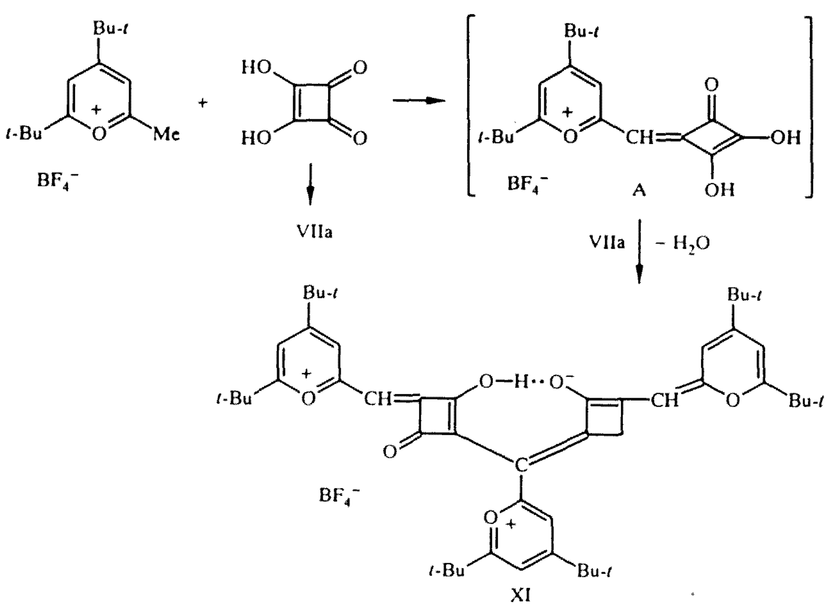


X

VII a—c $R^1 = R^2 =$ Bu-t; a X = O, b X = S, X = NMe; VIII $R^1 =$ Ph, $R^2 =$ Bu-t, X = O

In the condensation of 2,4-di(tert-butyl)-6-methylpyrylium perchlorate IIa with squaric acid, in addition to the squarylium dye VIIa, a dye absorbing in a longer-wave region, which, judging by the PMR spectrum, has the structure XI, is also formed. The reaction in this case evidently proceeds analogously to the interaction of 2-methyl-3-alkylbenzothiazolium salts with squaric acid [15]. At first a mixture of the usual squarylium dye VIIa and an intermediate product A are formed; the intermediate reacts with compound VIIa according to an electrophilic substitution reaction. In the case of γ-pyrylium derivatives, like 1,3,3-trimethylindolium derivatives [16], a trinuclear dye is not formed, possibly on account of the greater steric hindrances. The dyes synthesized are readily soluble in methylene chloride and aromatic hydrocarbons, and dissolve satisfactorily in acetonitrile and alcohols.

In the IR spectra of the dyes VIa—X, like other 1,3-type squarylium dyes [16], intense bands are observed in the region of ~1600 cm^{-1}, belonging to the stretching vibrations of the four-membered ring (C_4O_2), along with a rather intense band in the region of 1210-1250 cm^{-1}, characteristic of tert-butyl substituents. In the case of pyrylocyanines, moreover, bands are observed in the region of 1610-1640 cm^{-1} (the pyrylium ring) [17], whereas in thiopyrylocyanines bands are observed in the regions 1420-1495 cm^{-1} and 1530-1590 cm^{-1}, characteristic of the thiopyrylium cation [18]. This agrees with the structure assumed for dyes of this type, with a positive charge on the heterocyclic residues, and not on the squarylium fragment, as was



indicated in [16], although on account of the close positioning of the bands of the four-membered ring and heterocyclic rings, it is difficult to make a rigorous assignment of them. It is important that in the spectra of all the dyes there are no vibrations in the region of ~ 1700 cm^{-1}, characteristic of the $=C=O$ bond, which is an indication of its strong delocalization.

The nature of the PMR spectra of the compounds under consideration agrees with a coplanar centrosymmetrical structure of their molecules, which has been described by x-ray spectral analysis for their analog containing 1,3,3-trimethyl-3H-indoline residues as the terminal groups [19]. As a result of the low (in the PMR time scale) rate of rotation around the bonds of the chromophores situated between the heterocyclic residues and the squarylium ring, for dyes of the γ-series VIa,b, in contrast to the corresponding dicarbocyanines, a nonequivalence of the protons of the two tert-butyl groups and the two pairs of β-protons is observed. An analogous nonequivalence of the spectra of the β-protons, exceeding 2 ppm, is also observed in dyes of the α-series VIIa-c. In this case, if we compare the PMR spectra of compounds VI and VII with the spectra of the corresponding dicarbocyanines, for one of the pairs of β-H a weakly polar shift (~ 1.7-2.0 ppm) is observed, and for the other a strongly polar shift (~ 0.4-0.6 ppm). This effect should be explained by the strong interaction of one of the pairs of β-H with the oxygen atom of the central four-membered ring, similar to that observed in 2-dimethylaminothienyl-5- [20] and p-aminophenyl-substituted squaraines [21].

On the basis of the characteristic electronic absorption spectra of the dyes synthesized (Table 1) it follows that in most cases they are characterized by the same patterns in the color as in the series of analogous polymethine dyes with an unclosed chromophore. The dyes VII, constructed from single-ring heterocycles of the α-series, are more deeply colored and possess more diffuse absorption bands than their isomers VI of the γ-series. Thiopyrylium derivatives are more deeply colored than monotypic compounds of the pyrylium series, which, in turn, are more deeply colored than their pyridinium analogs. The absorption bands of the squaraines obtained and the dicarbocyanines corresponding to them differ little in intensity. Only for the pyridocyanine VIIc and the diphenyl-substituted pyrylocyanine VIII, evidently in view of the steric hindrance in their molecules, are the absorption bands appreciably less intense than for their analogs with an unsubstituted pentamethine chromophore (Δ logε ~0.32-0.33). The absorption bands of the dyes of the γ-series VIa,b obtained are narrower than those of the dicarbocyanines analogs to them, similar to what is observed for the corresponding quino-derivatives [8]. Thus, in methylene chloride the half-widths of the long-wave bands of compounds VIa and VIb are equal to 520 and 465 cm^{-1}, respectively, and for the corresponding dicarbocyanines 640 and 585 cm^{-1}. Such a comparison cannot be performed for dyes of the α-series on account of the pronounced vibrational nature of the bands. The squaraines obtained, as it follows from the bathochromic shift of their absorption bands in the transition from solutions in methylene chloride to solutions in the less polar hexane, are characterized by negative solvatochromism, i.e., their ground state is more polar than the excited state, just as for other dyes of this type [22].

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Gross formula	Found, % / calculated, %		mp, °C	Electronic spectrum, λ_{max}, nm (log ε) in CH_2Cl_2	PMR spectrum, δ, ppm, $CDCl_3$/HMDS	Yield, %
		C	H				
VIa	$C_{32}H_{42}O_4$			291...293	643 (4,62), 710 (5,48) [649 (4,73), 719 (5,44)]*	1,21 (18H, s, 2-C(CH$_3$)$_3$), 1,28 (18H, s, 6-C(CH$_3$)$_3$), 5,75 (2H, s, α-H), 6,13 (2H, s, β-H), 8,59 (2H, s, β'-H)	45
VIb	$C_{32}H_{42}O_2S_2$			268...270	725 (4,66), 812 (5,52) [725 (4,68), 814 (5,47)]	1,28 (18H, s, 2-C(CH$_3$)$_3$), 1,38 (18H, s, 6-C(CH$_3$)$_3$), 6,00 (2H, s, α-H), 6,85 (2H, c, β-H), 9,17 (2H, s, β'-H)	40
VIIa	$C_{32}H_{42}O_4$	78,5 78,3	8,8 8,6	202...204	671 (4,81), 732 (5,12) [681 (4,77), 745 (4,93)]	1,19 (18H, s, 4-C(CH$_3$)$_3$), 1,21 (18H, s, 6-C(CH$_3$)$_3$), 5,82 (2H, s, α-H), 6,01 (2H, s, β-H), 8,84 (2H, s, β'-H)	60
VIIb	$C_{32}H_{42}O_2S_2$	73,2 73,5	8,3 8,1	225...227	768 (4,70), 842 (4,90) [384 (3,82), 780 (4,75), 856 (4,86)]	1,26 (18H, s, 4-C(CH$_3$)$_3$), 1,27 (18H, s, 6-C(CH$_3$)$_3$), 6,17 (2H, s, α-H), 6,71 (2H, s, β-H), 8,97 (2H, s, β'-H)	38
VIIc	$C_{34}H_{48}N_2O_2$	79,0 79,0	9,6 9,4	Higher than 250	635 (4,50), 683 (5,02) [648 (4,66), 702 (5,11)]	1,26 (18H, s, 4-C(CH$_3$)$_3$), 1,41 (18H, s, 6-C(CH$_3$)$_3$), 3,58 (6H, s, NCH$_3$), 5,30 (2H, s, α-H), 6,37 (2H, s, β-H), 9,19 (2H, s, β'-H)	42
VIII	$C_{36}H_{34}O_4$	81,7 81,5	6,6 6,5	259...260	753 (4,71), 835 (4,84)		45
IX	$C_{32}H_{30}O_4$	80,1 80,3	6,5 6,3	251...253	691 (4,76), 770 (5,49)	1,40 (18H, s, C(CH$_3$)$_3$), 6,80 (2H, s, α-H), 7,38 (4H, m, Ar–H), 7,59 (2H, m, Ar–H), 8,08 (2H, m, Ar–H), 8,70 (2H, s, 3-H)	39
X	$C_{32}H_{30}O_4$	79,9 80,3	6,6 6,3	238...240	678 (4,83), 744 (5,13)	1,54 (18H, s, C(CH$_3$)$_3$), 6,13 (2H, s, α-H), 7,23 (4H, m, Ar–H), 7,44 (2H, m, Ar–H), 7,93 (2H, m, Ar–H), 9,03 (2H, s, 3-H)	47
XI	$C_{50}H_{63}BF_4O_7$			260...262	453 (4,15), 835 (5,22)	1,28 (18H, s, 4-C(CH$_3$)$_3$), 1,33 (18H, s, 6-C(CH$_3$)$_3$), 1,40 (9H, s, 4''-C(CH$_3$)$_3$), 1,43 (9H, s, 6''-C(CH$_3$)$_3$), 5,98 (2H, s, α-H), 6,64 (2H, s, β-H), 7,29 (1H, s, β''-H), 7,98 (1H, s, β''-H), 8,84 (2H, br. s, β'-H)	

---

*Data in n-hexane are shown in brackets.

However, the color of squaraines that are derivatives of pyrylium and thiopyrylium has an important peculiarity. For these dyes the absorption maxima are shifted not bathochromically but, on the contrary, hypsochromically in comparison with the maxima of dicarbocyanines. Evidently the deeper color of squaraines in comparison with dicarbocyanines [6, 8] is not a general pattern but is correct only for dyes containing residues of heterocycles possessing high or medium electron-donor capacity as the terminal groups. The opposite pattern is characteristic of dyes with residues of low electron-donor capacity. As electron-donor capacity decreases, with all other factors the same, the hypsochromic shift increases. For example, for thiopyrylium derivatives it is somewhat greater than for pyrylium derivatives; for dyes of the α-series it is greater than for γ-isomers. For the dye X, which contains the least electron-donor system of α-benzopyran, the greatest hypsochromic shift of the absorption bands (42 nm) is observed. The dye X proves to be more highly colored than its γ-isomer IX, in contrast to most of the pyrylocyanines, among which the α-isomers absorb more deeply than their γ-isomers.

Considering squaraines as dicarbocyanines substituted in the chromophore [8] is clearly insufficient to explain the patterns of their coloration. Actually, both substituents brought into the chromophore of dicarbocyanine by the squaric acid residue — the electron acceptor $=C=O$ substituent in even positions of the chromophore and the electron donor $-O^-$ in the odd positions — should induce a deepening of the color. The situation does not become clearer if in the same approach we consider the $C=O$ group not as a simple substituent but, which is more correct, as a bridge, since the latter should have only a slight (on account of the induction effect) influence on the color [23]. Evidently in explaining the dependence of the color of the type of dye under consideration on the nature of the terminal heterocyclic residues, we should proceed from the presence of two chromophore systems in their molecules: polymethine and a sterically stressed fragment C_4O_2, on which, according to the data of [24], an $S_0 \rightarrow S_1$ transition is concentrated for bis[4-(dimethylamino)phenyl]squaraines.

EXPERIMENTAL

The electronic absorption spectra of compounds VIa,b, VIIa-c, VIII, and XI were measured on a Specord M-400 spectrophotometer. The PMR spectra were obtained on a Bruker WP-200 spectrometer at 25°C, working frequency 200.132 MHz, internal standard hexamethyldisiloxane (HMDS). The IR spectra were taken on a UR-20 spectrometer in KBr tablets. The purity of the preparations was monitored by thin-layer chromatography on Merck Silicagel 60 F_{254} plates.

General Procedure for Producing Squaraines VIIa,b, VIIa,b, VIII-X. A mixture of 2 mmoles of the corresponding salt IIa,b, III-V, 1 mmole of squaric acid, 2 mmoles of quinoline in 10 ml of n-butanol, and 25 ml of absolute toluene was boiled with azeotropic removal of water. After cooling, 50 ml of toluene was added to the reaction mass, it was allowed to stand for 1 h, and the quinoline salt was filtered off. The solvent was removed from the filtrate under water-jet pump vacuum, and the residue was recrystallized from acetonitrile, with the exception of VIII, which was washed with boiling acetonitrile.

1-Methyl-2-{[3-[(1-methyl-4,6-di-tert-butyl-2H-pyridin-2-ylidene)-methyl]-2-oxido-4-oxo-2-cyclobuten-1-ylidene]methyl}-4,6-di-(tert-butyl)pyridinium (internal salt) (VIIc). To a solution of 0.5 mmoles of the squarylium dye VIIa in 5 ml of DMFA we added 1 ml (3 mmoles) of a 10% solution of methylamine in methanol; the mixture obtained was kept for 3 h at 120°C. After cooling it was diluted with water; the precipitate was filtered off and crystallized from acetonitrile.

The characteristics of the compounds obtained are shown in Table 1.

The work was conducted with partial financial support from the United Fund of the Government of Ukraine and the International Science Fund (Grant No. K2R100).

REFERENCES

1. M. A. Kudinova, E. I. Maiboroda, Yu. L. Slominskii, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 1, 96 (1996).
2. J. Fabian, H. Nakazumi, and M. Matsuoka, Chem. Rev., **92**, 1197 (1992).
3. K.-Y. Law, Chem. Rev., **93**, 449 (1993).
4. M. Emmelius, G. Pavloski, and H. Vollmann, Angew. Chem. Int. Ed. Engl., **28**, 1445 (1989).
5. M. Matsuoka, Infrared Absorption Dyes, Plenum Press, New York (1990).
6. T. N. Geraimova and V. V. Shelkovnikov, Usp. Khim., No. 6, 102 (1992).

7. M. R. Detty and B. Henne, Heterocycles, **35**, 1149 (1993).
8. S. Yasui, M. Matsuoka, and T. Kitao, Dyes and Pigments, **10**, 13 (1988).
9. V. V. Kudryukov, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 760 (1987).
10. M. A. Kudinova, V. V. Kudryukov, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 902 (1990).
11. M. A. Kudinova, V. V. Kurdyukov, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 3, 339 (1992).
12. H. E. Sprenger and W. Ziegenbein, Angew Chem., **79**, 581 (1967).
13. Japanese Patent No. 58,220,143; Chem. Abstr., **101**, 219727a (1984).
14. Japanese Patent No. 63,168,393; Chem. Abstr., **110**, 125550a (1989).
15. H. Nakazumi, K. Natukawa, K. Nakai, and K. Isagawa, Angew Chem. Int. Ed. Engl., **33**, 1001 (1994).
16. N. Kuramoto, K. Natsukawa, and K. Asao, Dyes and Pigments, **11**, 21 (1989).
17. A. T. Balaban, G. D. Mateescu, and M. Elian, Tetrahedron, **18**, 1083 (1962).
18. V. G. Kharchenko M. E. Stankevich, A. R. Yakoreva, and A. A. Rassudova, Khim. Geterotsikl. Soedin., No. 7, 916 (1972).
19. Y. Kobayashi, V. Gato, and M. Kurahashi, Bull. Chem. Soc. Jpn., **59**,311 (1986).
20. D. Keil, H. Hartmann, and T. Moschny, Dyes and Pigments, **17**, 19 (1991).
21. K. Law, F. C. Bailey, and L. J. Bluett, Canad. J. Chem., **64**, 1608 (1986).
22. S. Das, K. G. Thomas, R. Ramanathan, M. V. George, and P.V. Kamat, J. Phys. Chem., **51**, 1362 (1993).
23. A. D. Kachkovskii, Structure and Color of Polymethine Dyes [in Russian], Kiev, Naukova Dumka (1989).
24. R. W. Bigelow and H. J. Freund, J. Chem. Phys., **107**, 159 (1986).