PYRYLOCYANINES.

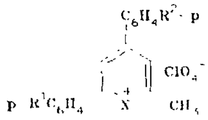
20.* SYMMETRICAL METHOXY-SUBSTITUTED TETRAPHENYLPYRYLOCYANINES AND THEIR HETEROANALOGS

I. M. Gavrilyuk, A. A. Ishchenko,
M. A. Kudinova, and A. I. Tolmachev

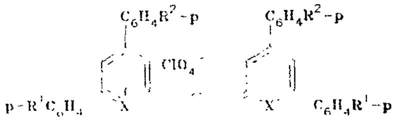
UDC 547.812.5'818.1'821.3:
541.651: 668.819

Symmetrical tetraphenyl-substituted α-pyrylo-, α-thiopyrylo-, and α-pyridotrimethylcyanines, containing electron donor methoxy groups in two or four phenyl rings, were synthesized. Using the methods of quantum chemistry, the characteristics of the long-wave absorption bands of the dyes obtained are discussed. The independence of the theoretical conclusions from the selection of the quantum chemical parameters was demonstrated. The hypothesis of greater participation of the carbon-carbon bonds of the oxygen- and especially the sulfur-containing heteroresidues in comparison with the nitrogen-containing residues in the general system of conjugation is confirmed.

Pyrylo-2-cyanines and their sulfur analogs are substantially more deeply colored, while pyrido-2-cyanines, on the contrary, are somewhat lighter than the dyes of isomeric structure, in which the heteroresidues are bonded to the chromophore in the 4-position [2]. We explained this fact qualitatively by the fact that in view of the smaller tendency for conjugation of the oxygen and sulfur atoms in comparison with the nitrogen atom in α-pyrylo- and especially α-thiopyrylocyanines, the carbon-carbon bonds of the heterocyclic residues participate more in the general system of conjugation than in α-pyridocyanines [2]. If this hypothesis is correct, then we should expect that substituents in the heteroresidues of α-pyrylocyanines will have a greater influence on the color than in their nitrogen analogs. The purpose of this work was the production and spectral investigation of methoxy-substituted tetraphenylpyrylo-, -thiopyrylo-, and -pyrido-2-cyanines for a verification of the indicated hypothesis. The synthesis was conducted on the basis of pyrylium (Ia-c) and thiopyrylium salts (IIa, b). The latter are formed under the action of a solution of NaSH on Ia, b. Symmetricl pyrylo- and thiopyrylotrimethylcyanines IIIa-c, IVa, b were produced by condensation of the indicated salts with the ethyl ester of orthoformic acid, while pyridocyanines Va-c were produced by the action of methylamine on the dyes IIIa-c.



Ia-c, IIa, b



IIIa-c, IVa, b, Va-c

I–V a, c $R^1=OCH_3$, b, c $R^2=OCH_3$; I, III X=O; II, IV X=S; V $X=NCH_3$; where not indicated, R^1, R^2=H

The spectral characteristics of solutions of the synthesized dyes in relatively nonpolar methylene chloride and strongly polar acetonitrile are compared with the analogous characteristics of unsubstituted dyes III-V in Table 1. Together with λ_{max} and log ε, just as in [1, 2], the average positions of the absorption bands M^{-1}, the forces of the oscillators f, and the characteristics of the shape of the bands – the width σ, coefficients of asymmetry γ_1, excess γ_2, and fine structure F, determined according to the methods of moments, are cited. Table 2 presents the average positions of the bands M_{theor}^{-1} calculated according to a simple HMO method and the quadratic changes in the bond orders during excitation δ [3]. The theoretical conclusions could be reliably compared with the experimental

---

*For communication 19, see [1].

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1486-1491, November, 1984. Original article submitted January 17, 1984.

0009-3122/84/2011-1226$08.50

TABLE 1. Characteristics of Long-Wave Absorption Bands of the Dyes III-V

Dye	X	R^1	R^2	Solvent*	λ_{max}, nm	lg ε	$\varepsilon_1/\varepsilon_2$	M^{-1}, nm	f	σ, cm^{-1}	γ_1	γ_2	F
III	O	H	H	1 [2]	730, 800	4,77; 4,93	0,69	739,6	0,78	1176	1,17	2,2	0,064
				2 [14]	725, 790	4,76; 4,80	0,89	721,6	0,77	1279	1,09	1,9	0,057
IIIa	O	CH_3O	H	1	746, 822	4,73; 4,92	0,65	764,6	0,72	1122	1,19	2,1	0,071
				2	738, 810	4,76; 4,82	0,87	743,1	0,78	1264	1,14	2,1	0,058
IIIb	O	H	CH_3O	1	734, 810	4,85; 5,05	0,63	753,8	0,90	1100	1,17	1,9	0,077
				2	728, 800	4,73; 4,82	0,80	735,7	0,70	1234	1,19	2,3	0,065
IIIc	O	CH_3O	CH_3O	1	746, 824	4,79; 5,02	0,59	769,5	0,80	1079	1,20	2,0	0,079
				2	740, 815	4,78; 4,88	0,78	749,9	0,79	1215	1,22	2,4	0,066
IV	S	H	H	1 [2]	865	4,85	—	820,2	0,79	1058	1,07	1,8	0,046
				2 [14]	838	4,72	—	786,9	0,69	1267	1,08	2,1	0,045
IVa	S	CH_3O	H	1	890	4,86	—	839,1	0,75	1089	1,19	2,5	0,050
				2	855	4,81	—	806,1	0,82	1329	1,40	4,2	0,059
IVb	S	H	CH_3O	1	890	4,86	—						
				2	858	4,80	—						
V	NCH_3	H	H	1 [2]	630	4,97	—	604,6	0,88	1060	1,00	2,0	0,041
				2	626	4,88	—	599	0,83	1230	1,22	2,9	0,058
Va	NCH_3	CH_3O	H	1	632	4,97	—	608	0,88	1130	1,20	2,8	0,052
				2	626	4,93	—	601	0,93	1230	1,22	2,8	0,057
Vb	NCH_3	H	CH_3O	1	628	4,97	—	606	0,82	1090	1,25	2,8	0,058
				2	625	4,95	—	600	0,90	1190	1,25	2,9	0,059
Vc	NCH_3	CH_3O	CH_3O	1	632	(4,79)	—	608	(0,56)	1140	1,35	3,4	0,067
				2	628	(4,73)	—	601	(0,61)	1250	1,36	3,5	0,071

*1) methylene chloride; 2) acetonitrile.

data only for pyrylocyanines IIIa-c and thiopyrylocyanines IVa. In pyridocyanines the bands of the first electronic transitions are overlapped to a substantial degree by the bands of the other transitions, while the absorption spectra of solutions of the dye IVb were measured with even lower accuracy, and therefore a determination of the moments was not meaningful for it [4].

The values of M_{theor}^{-1} and δ are cited for two different sets of quantum chemical parameters, taken from [5, 6]. The parameters of [5] satisfactorily describe the changes in the color [5] and the width of the bands [7, 8], but they poorly reflect the electron donor capacity of the terminal heterocyclic groups. Thus, the electron donor capacities of the heteroresidues in α-pyrylo- and α-pyridocyanines, calculated with their aid, differ by only 7.6°C [9], whereas from the value of the deviations [9] we should have expected a far greater difference. A calculation performed using the parameters of [6] leads to a satisfactory difference of the electron donor capacities of the heteroresidues in α-pyrylo- (φ = 36.7°) and α-pyridocyanines (φ = 64.2°). In view of the large difference in electron donor capacity of the heteroresidues of the dyes discussed in this work, the need arose for determining whether the tendency in the variation of the values of M_{theor}^{-1} and δ depends on the selection of parameters (in [7, 8] there was no such necessity, since for the terminal groups of the dyes discussed in them, the theory, in agreement with the experiment, predicted close electron donor capacity). From Table 1 it is evident that the values of the average positions and the quadratic changes in the bond orders obtained using the parameters of [5, 6] vary in correlation, despite the difference in the absolute values; consequently, the theoretical conclusions should not depend on the selection of the parameters. The influence of the methoxy group was simulated analogously [7, 8]. It was considered in this case that the introduction of this group into the phenyl ring leads to an increase in the order of the $C{-}C_6H_5$ bond [7, 8]. Therefore, for $C_{(4)}{-}C_6H_4OCH_3$-p bonds in all the heterocyclic residues and $C_{(6)}{-}C_6H_4OCH_3$-p in pyrylium nuclei, the resonance integral β was assumed equal to 1.0 instead of 0.8 [7], while for thiopyrylocyanines it varied from 0.6 (as was assumed for the unsubstituted dye IV) to 0.9. Only for pyridocyanines, in the molecules of which the phenyl group under consideration is at an angle of 60° [10] relative to the plane of the chromophore, and its rotation is hindered as a result of strong steric hindrances, the resonance integral of the bond $C_{(6)}{-}C_6H_4OCH_3$-p was assumed equal to 0.5, just as for the unsubstituted dye V.

From the results of quantum chemical calculations we should have expected that the introduction of methoxy groups into α-pyrylocyanine III should lead to a deepening of the color; moreover, the effect from substitution should decrease in the sequence IIIc > IIIa > IIIb.

TABLE 2. Results of Quantum Chemical Calculations

Dye	Parameters [5]		Parameters [6]	
	M_{theor}^{-1}, nm	δ	M_{theor}^{-1}, nm	δ
III	671,1	0,1762	797,3	0,1723
IIIa	691,4	0,1746	827,1	0,1672
IIIb	687,8	0,1725	815,2	0,1668
IIIc	706,9	0,1705	842,5	0,1619
IV	744,0	0,1630	871,0	0,1509
IVa*	741,5	0,1616	868,3	0,1495
IVa**	761,6	0,1629	899,2	0,1507
IVa***	773,7	0,1637	906,3	0,1508
IVb	759,8	0,1600	886,0	0,1749
V	643,8	0,1656	604,5	0,1693
Va	642,0	0,1649	602,1	0,1685
Vb	659,3	0,1633	621,1	0,1676
Vc	658,1	0,1626	618,8	0,1668

*$\beta[C_{(6)}{-}C_6H_4OCH_3\text{-}p] = 0.6\beta$. **$\beta[C_{(6)}{-}C_6H_4OCH_3\text{-}p] = 0.8\beta$. ***$\beta[C_{(6)}{-}C_6H_4OCH_3\text{-}p] = 0.9\beta$.

Actually, according to Table 1, the experimental values of M^{-1} and λ_{max} of the investigated pyrylocyanines in both solvents vary in the indicated sequence. Thiopyrylium dyes IVa, b, just as should have been expected from the calculation, are also more deeply colored than the unsubstituted trimethylcyanine IV; moreover, the deepening of the color in the sequence from IV to IVb exceeds the analogous change for the corresponding oxygen-containing heteroanalog. This confirms the earlier hypothesis [2] that the greatest participation of the carbon-carbon bonds of the heteroresidues in the general system of conjugation in the series of thiopyrylo-, pyrylo-, and pyrido-2-cyanines should be expected precisely for sulfur-containing dyes of the structure under discussion. The smaller influence of the substituent in the thiopyrylotrimethylcyanine molecule IVa (according to the change in M^{-1}) in comparison with the oxygen of the heteroanalog IIa can evidently be explained by the fact that complete flattening of the molecule at the $C_{(6)}{-}C_6H_4OCH_3\text{-}p$ bond does not occur as a result of the larger size of the sulfur atom. We observed an analogous phenomenon in the case of methoxy-substituted triflavylocyanines [8]. According to the calculations, methoxysubstituents should have a weaker influence on the color of the pyridocyanine V. Actually, the experimental values of M^{-1} and λ_{max} are virtually unchanged in this case when methoxy groups are introduced. This interesting fact also confirms the hypothesis that in α-pyridocyanines the carbon–carbon bonds of the heterocycles participate substantially less in conjugation than in their oxygen analogs and especially their sulfur analogs.

Let us consider further the patterns in the width and shape of the absorption bands of the investigated dyes. For pyrylocyanines, just as we should have expected from the results of quantum chemical calculations of the values of δ, the introduction of methoxy groups leads to narrowing of the bands, which is a maximum for the tetramethoxy-substituted dye IIIc. The introduction of methoxy groups into the unsubstituted thiopyrylocyanine molecule (dye IVa) leads to a broadening of the absorption band, in accordance with the theory. The correlated variation of the quantities δ and σ in the case of pyrylo- and thiopyrylocyanines when methoxy substituents are introduced indicates that the narrowing of the bands in the case of substitution (for the dye IVa – broadening) is due primarily to the corresponding change in the value of the vibron interactions. This conclusion is also confirmed by the fact that in the series III, IIIa-c, the narrowing of the bands is accompanied by a decrease in the intensity ratio ($\varepsilon_1/\varepsilon_2$) of the vibrational and fundamental maxima, an enhancement of the structuring (increase in F), and, as a rule, an increase in the asymmetry and excess (increase in γ_1 and γ_2). The influence of methoxy groups on the width of the bands of pyrylocyanines IIIa-c can be explained by the fact that these groups primarily increase the electron donor capacity of the terminal heterocyclic residues and gradually bring them closer to rings of medium basicity. This should be accompanied by an evening out of the bond orders in the chromophore chain. The broadening of the absorption band of the thiopyrylium dye IVa can evidently be explained by the fact that together with the increase in the basicity of α-thiopyranylidene rings, the methoxy groups, when introduced into the molecule of IV, exert a stronger perturbing influence as a result of the greater participation of the oxygen–carbon bonds of the sulfur-containing heteroresidue in the system of conjugation. The patterns noted in the width and shape of the absorption bands of pyrylo- and thiopyrylocyanines are

TABLE 3. Characteristics of the Compounds Synthesized

Compound	T. dec., °C*	Found, %			Gross formula	Calculated, %			Yield, %
		C (N)	H (S)	Cl		C (N)	H (S)	Cl	
Ia	200—202	60,7	4,4	9,2	$C_{19}H_{17}ClO_6$	60,6	4,5	9,4	10
Ib	213—214	60,7	4,2	9,2	$C_{19}H_{17}ClO_6$	60,6	4,5	9,4	15
IIa	178—179		(8,2)	9,0	$C_{19}H_{17}ClO_5S$		(8,2)	9,0	38
IIb	186—187		(8,2)	9,0	$C_{19}H_{17}ClO_5S$		(8,2)	9,0	30
IIIa	195—196	70,3	4,7	5,1	$C_{39}H_{31}ClO_8$	70,6	4,7	5,4	25
IIIb	255—256	70,7	4,7	5,2	$C_{39}H_{31}ClO_8$	70,6	4,7	5,4	10
IIIc	240—242	68,2	4,5	4,8	$C_{41}H_{35}ClO_{10}$	68,1	4,8	4,9	20
IVa	237—238		(9,4)	5,0	$C_{39}H_{31}ClS_2O_6$		(9,2)	5,1	10
IVb	196—198		(9,2)	5,0	$C_{39}H_{31}ClS_2O_6$		(9,2)	5,1	8
Va	230—231	(4,1)		5,2	$C_{41}H_{37}ClN_2O_6$	(4,1)		5,2	36
Vb	227—229	(4,4)		5,2	$C_{41}H_{37}ClN_2O_6$	(4,1)		5,2	50
Vc	166—168	(3,7)		4,6	$C_{43}H_{41}ClN_2O_8$	(3,7)		4,7	46

*Compounds Ia, Ib, IIa, and IIb were crystallized from CH_3COOH, IIIa-c IVa, and IVb from CH_3CN, Va-c from CH_3CN–C_2H_5OH (2:3).

observed both in relatively nonpolar methylene chloride and in highly polar acetonitrile; however, in the latter the effects from substitution are somewhat less pronounced.

Thus, on the example of methoxy-substituted α-pyrylo-, α-thiopyrylo-, and α-pyridotrimethylcyanines, the earlier hypothesis [2] of greater participation of carbon-carbon bonds of sulfur- and oxygen-containing heteroresidues in the system of conjugation of the dyes than in the case of nitrogen-containing heterocyclic nuclei, advanced earlier [2], is confirmed. Independence of the theoretical conclusions from the selection of the quantum chemical parameters was demonstrated.

EXPERIMENTAL

The moments of the absorption bands were determined analogously to [1] on the basis of the absorption spectra of the dyes, recorded on an SF-4A spectrophotometer in methylene chloride, stabilized with 1% C_2H_2OH, and acetonitrile. The UV spectra of the salts were measured on the same instrument in acetonitrile. The PMR spectra were determined on a Tesla BS-487-B spectrometer with a working frequency 60 MHz at 20°C in CF_3COOH, internal standard HMDS. The purity of the preparations was monitored by the method of thin-layer chromatography on Silufol UV-254 plates. The eluent was nitromethane (for α-pyridocyanines — acetonitrile).

2-Methyl-4-phenyl-6-(4-methoxyphenyl)pyrylium perchlorate (Ia, Table 3). To a solution of 4.79 g (33 mmoles) benzalacetone in 30 ml of absolute ether, cooled to 0°C, 4.1 ml (50 mmoles) 70% $HClO_4$ and 5.4 g (36 mmoles) p-methoxyacetophenone were added dropwise, and 22 ml of acetic anhydride was added dropwise with mixing and continuous cooling. The salt Ia is isolated after exposure of the reaction mixture at room temperature for 4-5 h. UV spectrum, λ_{max}, nm (log ε): 275 (4.20); 328 (4.24), 418 (4.36). PMR spectrum: 2.44 (3H, s, CH_3), 3.42 ppm (3H, s, OCH_3).

2-Methyl-4-(4-methoxyphenyl)-6-phenylpyrylium perchlorate (Ib). To a suspension of 4.76 g (20 mmoles) anisalacetophenone [11] in 18 ml absolute ether, cooled to 0°C, 2.41 ml (30 mmoles) of 70% $HClO_4$ was added dropwise, then, cooling continuously, 13 ml of acetic anhydride was added. In this case a red crystalline precipitate was formed. The reaction mixture was heated to room temperature, 1.1 ml (∿20 mmoles) of very special purity acetone was added, and the mixture was boiled on a water bath until the above-mentioned precipitate dissolved completely. The salt Ib is isolated after exposure of the reaction mixture at room temperature for 4-5 h. UV spectrum, λ_{max}, nm (log ε): 250 (4.25), 350 (4.22), 400 (4.58). PMR spectrum: 2.43 (3H, s, CH_3), 3.40 ppm (3H, s, OCH_3).

2-Methyl-4-phenyl-6-(4-methoxyphenyl)thiopyrylium perchlorate (IIa). To a suspension of 0.1 g (0.3 mmole) of the salt Ia in 2 ml of very special purity acetone, 1 ml of an aqueous alcohol solution of NaSH was added with mixing [12]. After mixing for 0.5 h at room temperature, the mixture was filtered into 0.6-0.8 ml (∿8 mmoles) of 70% $HClO_4$, and 150-200 ml of ether was added to precipitate the salt IIa. UV spectrum, λ_{max}, nm (log ε): 260 (3.89), 300 (4.07), 3.55 (4.20), 430 (4.21). PMR spectrum: 2.66 (3H, s, CH_3), 3.54 ppm (3H, s, OCH_3).

2-Methyl-4-(4-methoxyphenyl)-6-phenylthiopyrylium perchlorate (IIb) was produced analogously from the salt Ib. UV spectrum, λ_{max}, nm (log ε): 258 (4.21), 3.70 (3.89, point of inflection), 421 (4.20). PMR spectrum: 2.72 (3H, s, CH_3), 3.62 ppm (3H, s, OCH_3).

2-{3-[4-Phenyl-6-(4-methoxyphenyl)pyranylidene-2]-1-propenyl}-4-phenyl-6-(4-methoxyphenyl)pyrylium perchlorate (IIIa). A mixture of 0.376 g (1 mmole of the salt Ia, 4 ml of glacial CH_3COOH, 4 ml of acetic anhydride, 0.091 g (1 mmole) of anhydrous CH_3COONa, and 0.2 ml (3 mmoles) of orthoformic ester were heated at 130°C for 4 h. The precipitate of the dye was removed by filtration.

2-{3-[4-Phenyl-6-(4-methoxyphenyl)thiopyranylidene-2]-1-propenyl}-4-phenyl-6-(4-methoxyphenyl)tripyrylium perchlorate (IVa) was synthsized analogously from the salt IIa.

2-{3-[4-(4-Methoxyphenyl)-6-phenylpyranylidene-2]-1-propenyl}-4-(4-methoxyphenyl)-6-phenylpyrylium (IIIb), 2-{3-[4,6-di(4-methoxyphenyl)-pyranylidene-2]-1-propenyl}-4,6-di(4-methoxyphenyl)pyrylium (IIIc), and 2-{3-[4-(4-methoxyphenyl)-6-phenylthiopyranylidene-2]-1-propenyl}-4-(4-methoxyphenyl)-6-phenylthiopyrylium (IVb) perchlorates were synthesized analogously to the dye IIIa from the salts Ib, Ic [13], and IIb, respectively, in pyridine, pyridine, and acetic anhydride.

2-{3-[4-Phenyl-6-(4-methoxyphenyl)-1,2-dihydropyridinylidene-2]-1-propenyl}-4-phenyl-6-(4-methoxyphenyl)pyridinium perchlorate (Va). A 0.2 g (0.3 mmole) portion of the dye IIIa was dissolved in 5-7 ml of DMFA, 1 ml (∿25 mmoles) of 7.5% methanol solution of methylamine was added, and the mixture was heated at 50-60°C for 1.5 h, after which it was precipitated with water.

2-{3-[4-(4-Methoxyphenyl)-6-phenyl-1,2-dihydropyridinylidene-2]-1-propenyl}-4-(4-methoxyphenyl)-6-phenylpyridinium (Vb) and 2-{3-[4,6-di(4-methoxyphenyl)-1,2-dihydropyridinylidene-2]-1-propenyl}-4,6-di-(4-methoxyphenyl)pyridinium (Vc) perchlorates were synthesized analogously from the dyes IIIb and IIIc.

LITERATURE CITED

1. M. A. Kudinova, V. V. Kudryukov, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterosikl. Soedin., No. 4, 451 (1984).
2. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 898 (1980).
3. A. A. Ishchenko, N. A. Derevyanko, M. A. Kudinova, G. G. Dyadyusha, and A. I. Tolmachev, Teor. Éksp. Khim., 13, 828 (1977).
4. G. G. Dyadyusha and A. A. Ishchenko, Zh. Prikl. Khim., 30, No. 6, 1037 (1979).
5. A. I. Tolmachev, G. G. Dyadyusha, E. F. Karaban, A. A. Ishchenko, and N. A. Derevyanko, Khim. Geterotsikl. Soedin., No. 6, 739 (1978).
6. T. Tani, J. Phot. Sci., 19, 161 (1971).
7. I. M. Gavrilyuk, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 3, 304 (1983).
8. I. M. Gavrilyuk, A. A. Ishchenko, M. A. Kudinova, and A. I. Tolmachev, Ukr. Khim. Zh., 50, 1101 (1984).
9. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 903 (1980).
10. A. I. Tolmachev, M. Yu. Kornilov, L. M. Shulezhko, and A. V. Turov, Teor. Éksp. Khim., 11, 556 (1975).
11. C. Kohler, J. Am. Chem. Soc., 39, 1702 (1917).
12. G. A. Reynolds, Synthesis, 10, 638 (1975).
13. G. N. Dorofeenko and S. V. Krivun, Ukr. Khim. Zh., 29, 1058 (1963).
14. A. I. Tolmachev, N. A. Derevyanko, and A. A. Ishchenko, Khim. Geterotsikl. Soedin., No. 9, 1178 (1982).