

PYRYLOCYANINES.

VIII.* TETRAALKYL-SUBSTITUTED 4-PYRYLOCYANINES

A. I. Tolmachev, G. G. Dyadyusha, E. F. Karaban, UDC 547.813'829:541.651:668.819.45
A. A. Ishchenko, and N. A. Derevyanko

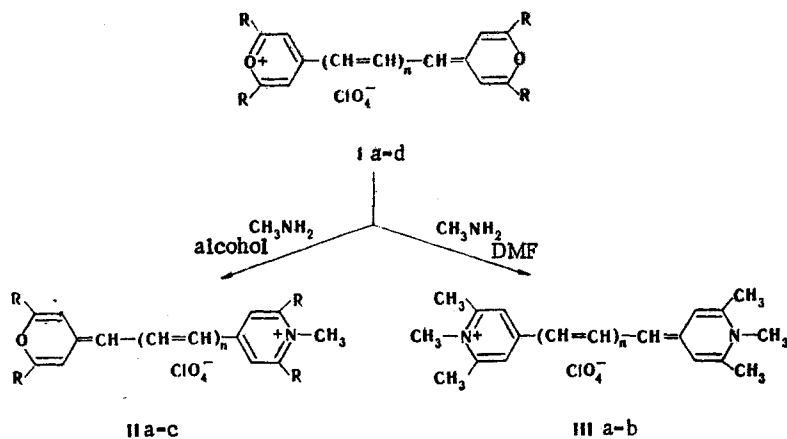
Tetraalkyl-substituted 4-pyrylocyanines were synthesized and converted to pyridocyanines by reaction with methylamine. The exchange reaction proceeds particularly readily in the series of tetramethyl-substituted compounds, in which the oxygen atoms in one or both pyrylium residues can be replaced, depending on the conditions. It was established that, in contrast to the tetraphenyl-substituted compounds, among the tetramethyl-substituted compounds the symmetrical dyes (pyridinium derivatives) are more deeply colored than their oxygen-containing analogs. The reasons for this difference in the absorption spectra are analyzed thoroughly by the quantum-chemical method.

One of the cardinal problems in the theory of the color of pyrylocyanine dyes and their analogs is the dependence of the position of the absorption band on the nature of the heteroatom [1]. On the basis of the spectra of the well-studied 2,6,2',6'-tetraphenyl-substituted 4-pyrylo- and 4-pyridocyanines [2], one might have concluded that the oxygen-containing derivatives should be more deeply colored than the nitrogen-containing derivatives; however, quantum-chemical estimates enable one to expect heightening of the color as the electronegativity of the heteroatom increases. The reason for this disagreement could be the different degree of conjugation of the α -phenyl groups with the pyrylium and N-methylpyridinium rings. The PMR spectra provide evidence that the 2-phenylpyrylium cations are virtually coplanar [3], whereas the interplanar angle reaches 60° in N-phenylpyridinium cations [4]. In fact, the difference in the color of pyrylo- and pyridocyanines decreases in the case of partial replacement of the phenyl groups by methyl groups [2], and the only known (up until now) tetramethyl-4-pyrylomonomethylidynecyanine (Ia) [5] is more highly colored than unsubstituted N,N'-diethyl-4-pyridomonomethylidynecyanine [6]. Unsubstituted pyrylocyanines are inaccessible. It therefore seemed of interest to make a detailed study of tetraalkylpyrylocyanines and their absorption spectra under comparable conditions with the analogous nitrogen-containing dyes.

2,6,2',6'-Tetramethyl-4-pyrylotrimethylidynecyanine (Ib) was synthesized by condensation of 2,4,6-trimethylpyrylium perchlorate with ethyl formate. A methyl group in the 4 position of the pyrylium ring has greater nucleophilic activity than methyl groups in the 2 and 6 positions [5], and one therefore should have expected the formation of a dye with precisely the structure presented in this reaction. The data from the PMR spectrum of pyridotrimethylidynecyanine IIb, obtained from Ib, constitute evidence in favor of this assumption.

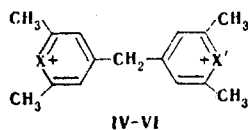
Analogous Ic, d of trimethylidynecyanine Ib, which contains isopropyl or tert-butyl groups, were similarly synthesized. Unsymmetrical pyrylopyridocyanines IIa, b were obtained by treatment of the pyrylocyanines with methylamine in aqueous methanol, whereas symmetrical pyridocyanines IIIa and IIIb were obtained in dimethylformamide (DMF). Thus we found that tetramethyl-substituted pyrylocyanines behave like tetraphenyl-substituted pyrylocyanines [2] with respect to methylamine. Stepwise exchange of the oxygen atoms in the pyrylocyanines is rigorously confirmed by the results of elementary analysis and the electronic and PMR spectra. The spectra of monomethylidynecyanines Ia-IIIa in trifluoroacetic acid, in which the compounds are protonated to give dications with IV-VI structures, present a particularly distinct pattern; the spectra consist exclusively of singlets [IV: 7.94 (4H), β -H of the

*See [1] for communication VII.



I-II a $n=0$, $R=CH_3$; b $n=1$, $R=CH_3$; c $n=1$, $R=CH(CH_3)_2$; I d $n=1$, $R=C(CH_3)_3$;
IIIa $n=0$; b $n=1$

pyrylium rings, 4.80 (2H), methylene group protons, and 3.02 ppm (12H), α -CH₃ groups; V: 7.84 (2H), β -H of the pyrylium ring, 7.73 (2H), β -H of the pyridinium ring, 4.54 (2H), methylene group protons, 4.16 (3H), NCH₃ group, 2.96 (6H), α -CH₃ groups of the pyrylium ring, and 2.86 ppm (6H), α -CH₃ groups of the pyridinium ring; VI: 7.63 (4H), β -H of the pyridinium rings, 4.40 (2H), methylene group protons, 4.11 (6H), NCH₃ group, and 2.82 ppm (12H), α -CH₃ groups of the pyridinium rings]. In contrast to tetramethyl-substituted pyrylocyanines, the oxygen atom in only one of the heterocyclic residues could be replaced in tetraisopropyl-substituted dye Ic, whereas dye Id, which contains tert-butyl groupings [7], does not react at all with methylamine. This decrease in reactivity is evidently due to steric factors.



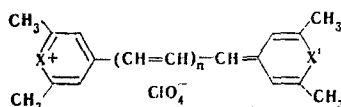
IV $X=X'=O$; V $X=O$, $X'=NCH_3$; VI $X=X'=NCH_3$

The absorption spectra of the various tetraalkyl-4-pyrylocarbocyanines are similar to one another. For example, λ_{max} (log ϵ) Ib 588 nm, Ic 595 nm (5.32), and Id 598 nm (5.30) in nitromethane. The difference between the λ_{max} values is even smaller in methylene chloride (λ_{max} Ib 595 nm, Ic 600 nm, and Id 600 nm). This indicates the insignificance of the effects of alkyl groups. A comparison of the absorption spectra of N,N'-dimethyl-4-pyridocarbocyanine (λ_{max} 603 nm in nitromethane and 613 nm in methylene chloride) and hexamethyl derivatives IIIb also provides evidence for the same conclusion (see Table 1). It is apparent that methyl groups in the 2,6,2',6' positions even display a weak hypsochromic shift. The detailed spectral characteristics of the methyl derivatives are presented in Table 1. In addition to the long-wave absorption maxima and the maximum values of the extinction coefficients, the oscillator forces (f), the average positions of the absorption bands (M^{-1}), the characteristics of the form of the band [the widths (σ), the asymmetry coefficients (γ_1), and the steepness (γ_2)] determined by the method of moments [8], and the coefficients of the fine structure (F) determined from the entropies of the spectral distributions [9] are also presented in Table 1.

It is apparent from Table 1 that with respect to the form and width of the absorption bands, the symmetrical dyes with nitrogen and oxygen atoms are similar to one another and undergo similar changes when the solvent is replaced. The bands are somewhat broader, more symmetrical, and more diffuse in nitromethane, which is a strong solvating solvent. The unsymmetrical dyes, which display considerable deviations (up to 100 nm), are distinguished by greater band widths and diffuse character, and their parameters are even more sensitive to the solvent. In contrast to the symmetrical dyes, the widths and diffuse character increase as the polymethyldiyne chain becomes longer in the case of the unsymmetrical dyes.

In view of the similarity in the form of the absorption bands, the absorption maxima of the symmetrical dyes with minimal distortions convey the regular shifts of the average positions of the bands as the solvent is replaced and as the oxygen atoms are replaced by nitrogen atoms. From the data in Table 1, one can state with confidence that, all other conditions

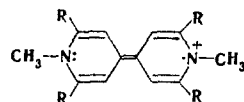
TABLE 1. Characteristics of the Long-Wave Absorption Bands of Cyanines Ia,b-IIIa,b



Ia,b - IIIa,b

Compound	n	X, X'	Solvent	λ_{max} , nm (lg ϵ)	M ⁻¹ , nm	f	σ , cm ⁻¹	γ_1	γ_2	F
Ia	0	O, O	CH ₂ Cl ₂	472 (5,02)	468,4	0,67	935	—	—	0,0948
			CH ₃ NO ₂	472 (5,00)	464,2	0,69	972	—	—	0,0664
IIa	0	NCH ₃ , O	CH ₂ Cl ₂	450 (4,75)	432,7	0,75	1452	1,15	2,5	0,0454
			CH ₃ NO ₂	437 (4,64)	420,3	0,70	1589	1,00	1,7	0,0362
IIIa	0	NCH ₃ , NCH ₃	CH ₂ Cl ₂	485 (5,11)	479,4	0,79	842	1,27	3,4	0,0518
			CH ₃ NO ₂	481 (5,04)	473,6	0,69	870	1,19	3,1	0,0532
Ib	1	O, O	CH ₂ Cl ₂	595	579,6	—	790	1,59	3,6	0,1370
			CH ₃ NO ₂	588	573,4	—	850	1,44	3,2	0,1207
IIb	1	NCH ₃ , O	CH ₂ Cl ₂	518 (4,70)	504,4	0,83	1741	1,11	2,2	0,0444
			CH ₃ NO ₂	495 (4,65)	481,1	0,85	1901	0,88	1,5	0,0270
IIIb	1	NCH ₃ , NCH ₃	CH ₂ Cl ₂	610 (5,30)	593,8	0,97	717	1,66	4,1	0,1018
			CH ₃ NO ₂	598 (5,11)	581,2	0,75	747	1,45	3,2	0,0872

being equal, the pyridocyanes are ~10 nm more deeply colored than the pyrylocyanines. Quantum-chemical estimates by the Hückel MO method lead to shifts of the same order of magnitude (calculated λ values: Ia 454, Ib 568, IIIa 475, and IIIb 581 nm). In this case the exceptionally deep color of the tetraphenylpyrylocyanine dyes should be ascribed to the coplanarity of the molecule. If one takes into account the resonance integral between the rings ($\beta_{C-Ph} = 0.8\beta$), tetraphenylation should give rise to a bathochromic shift on the order of 90 nm (the calculated λ_{max} values for $n = 0$ and $n = 1$ are, respectively, 542 and 658 nm), and this is actually observed (M_{exp}^{-1} , $n = 0$, 540.2 nm; $n = 1$, 665.1 nm). A shift of the same magnitude should also have been observed in the case of tetraphenylpyridocyanines if their molecules could be situated in a single plane. If one takes into account the fact that the steric hindrance between the α -phenyl groups and the methyl group attached to the nitrogen atom will lead to 60° rotation of these rings and it is assumed that β_{C-Ph} decreases to 0.5 β in this case, the effect of phenylation amounts to ~35 nm (the calculated λ_{max} values for $n = 0$ and $n = 1$ are, respectively, 511 and 616 nm); this is in good agreement with the experimental values (M_{exp}^{-1} , $n = 0$, 510.5 nm; $n = 1$, 630.5 nm). We note that similar steric factors are also invoked to explain the considerably smaller decrease in the bathochromic effect on replacement of the methyl groups by phenyl groups in nitrogen-containing cations radicals with VIIa, b structures ($\Delta\lambda = 35$ nm) than in the case of their oxygen-containing analogs ($\Delta\lambda = 189$ nm) [10].



VII a R = CH₃; b R = C₆H₅

EXPERIMENTAL

The electronic absorption spectra of $8 \cdot 10^{-6}$ to $2 \cdot 10^{-5}$ mole/liter solutions of the compounds were recorded at layer thickness of 1 cm and 5 cm as in [11] with an SF-4A spectrophotometer. The absorption spectra were subjected to mathematical treatment with the program in [9]. The PMR spectra of CF₃COOH solutions of the compounds were recorded with a Tesla BS-487-B spectrometer (80 MHz) at 20°C with tetramethylsilane as the internal standard. The quantum-chemical calculations were made with an ELA program and the following parameters: $\alpha_O = \alpha_C + 2.4\beta$, $\alpha_N = \alpha_C + 1.1\beta$, $\beta_{CC} = \beta = -26520$ cm⁻¹, $\beta_{CO} = 1.05\beta$, $\beta_{CN} = 0.83\beta$, and $\beta_{C-CH_3} = 0$.

The purity of the preparations was monitored by thin-layer chromatography on plates with a fixed layer of Silufol-254 silica gel and elution with nitromethane.

TABLE 2. Characteristics of the Synthesized Dyes

Compound	mp, °C	Found, %	Empirical formula	Calc., %	Yield, %
Ib	247	Cl 10.3	C ₁₇ H ₁₉ ClO ₆	Cl 10.0	77
Ic	178	Cl 7.6	C ₂₅ H ₃₅ ClO ₆	Cl 7.6	90
IIa	211	C 56.3; H 5.9; Cl 10.4	C ₁₆ H ₂₀ ClNO ₅	C 56.2; H 5.9; Cl 10.4	64
IIb	260	Cl 9.8; N 4.2	C ₁₈ H ₂₂ ClO ₅ N	Cl 9.7; N 4.4	74
IIc	118	Cl 7.5	C ₂₆ H ₃₈ ClNO ₅	Cl 7.4	66
IIIa	223	Cl 9.8; N 8.0	C ₁₇ H ₂₃ ClN ₂ O ₄	Cl 10.0; N 7.9	35
IIIb	195	Cl 9.2; N 7.5	C ₁₉ H ₂₅ ClN ₂ O ₄	Cl 9.3; N 7.4	42

2,6-Dimethyl-4-[3-(2,6-dimethyl-4H-pyranylidene)propen-1-yl]pyrylium Perchlorate (Ib). A mixture of 3.3 g (15 mmole) of 2,4,6-trimethylpyrylium perchlorate, 3 ml of ethyl orthoformate, 0.53 g (7.5 mmole) of anhydrous sodium acetate, and 15 ml of acetic acid was heated at 110°C for 30 min, and the precipitated dye was removed by filtration and washed with acetic acid and ether. It was then chromatographed on aluminum oxide (elution with acetonitrile), reprecipitated from acetonitrile by the addition of 20% HClO₄, and crystallized from glacial acetic acid (Table 2).

2,6-Diisopropyl-4-[3-(2,6-diisopropyl-4H-pyranylidene)propen-1-yl]pyrylium Perchlorate (Ic). A mixture of 0.505 g (2 mmole) of 2,6-diisopropyl-4-methylpyrylium perchlorate [13], 1 ml of ethyl orthoformate, 0.082 g (1 mmole) of anhydrous sodium acetate, and 4 ml of a mixture of acetic anhydride and acetic acid (1:1) was heated at 110°C for 5 min, after which it was cooled and treated with a saturated solution of sodium perchlorate. The precipitated dye was purified by reprecipitation from acetic acid by the addition of an aqueous solution of sodium perchlorate.

1,2,6-Trimethyl-4-[(2,6-dimethyl-4H-pyranylidene)methyl]pyridinium Perchlorate (IIa). A 0.5-ml sample of a 25% aqueous solution of methylamine was added to a solution of 0.328 g (1 mmole) of monomethylidyne Ia [5] in 10 ml of 50% aqueous methanol, and the mixture was stirred for 2 min. It was then diluted with 20 ml of water and made weakly acidic with 20% HClO₄. The solution was cooled to 0°C, and the precipitated dye was removed by filtration and purified by chromatography from a mixture of chloroform and nitromethane (1:1) on aluminum oxide and by crystallization from glacial acetic acid.

1,2,6-Trimethyl-4[3-(2,6-dimethyl-4H-pyranylidene)propen-1-yl]pyridinium Perchlorate (IIb). A solution of 0.2 g (0.6 mmole) of pyrylotrimethylidyne cyanine Ib and 0.2 ml of a saturated methanol solution of methylamine was refluxed for 5 min. The end of the reaction was monitored by spectrophotometry. The mixture was cooled, and the precipitated dye was removed by filtration and purified by chromatography on aluminum oxide (elution with nitromethane).

1-Methyl-2,6-diisopropyl-4-[3-(2,6-diisopropyl-4H-pyranylidene)propen-1-yl]pyridinium Perchlorate (IIc). A solution of 0.466 g (1 mmole) of pyrylotrimethylidyne cyanine Ic and 0.5 ml of a saturated solution of methylamine in methanol was heated in 4 ml of acetonitrile at 60°C for 5 min, after which it was cooled, and the dye was precipitated by the addition of a solution of sodium perchlorate and reprecipitated from alcohol.

1,2,6-Trimethyl-4-[(1,2,6-trimethyl-1,4-dihydropyridinylidene)methyl]pyridinium Perchlorate (IIIa). A mixture of 0.328 g (1 mmole) of monomethylidyne cyanine Ia, 3 ml of a saturated alcohol solution of methylamine, and 2 ml of dimethylformamide was heated at 100°C for 3 h, after which it was cooled and treated with water, and the precipitated dye was removed by filtration and purified by chromatography on aluminum oxide [elution with chloroform-acetonitrile (5:1)].

2,6-Dimethyl-4-[3-(2,6-dimethyl-1,4-dihydropyridinylidene)propenyl]pyridinium Perchlorate (IIIb). A mixture of 0.36 g (1 mmole) of pyrylotrimethylidenecyanine Ib and 0.4 ml of a saturated alcohol solution of methylamine in 8 ml of DMF was heated at 70°C for 30 min. The following day, the dye was removed by filtration and washed with ether. PMR spectrum (in CF₃COOH) of the dication formed from dye IIIb: 7.67 (2H, s) and 7.62 (2H, s) (β, β'-H of the pyridinium rings), 4.15 (3H, s, N-CH₃) and 4.10 (3H, s, N-CH₃), 3.93 and 3.85 (2H, d, CH₂), 2.87 (6H, s, α-CH₃ groups of the pyridinium rings), and 2.82 ppm (6H, s, α-CH₃).

LITERATURE CITED

1. A. I. Tolmachev, N. A. Derevyanko, and M. A. Kudinova, *Khim. Geterotsikl. Soedin.*, No. 5, 617 (1975).
2. A. I. Tolmachev, N. A. Derevyanko, E. F. Karaban, and M. A. Kudinova, *Khim. Geterotsikl. Soedin.*, No. 5, 612 (1975).
3. A. I. Tolmachev, L. M. Shulezhko, and M. Yu. Kornilov, *Ukr. Khim. Zh.*, 40, 286 (1974).
4. M. Yu. Kornilov, L. M. Shulezhko, and A. I. Tolmachev, *Teor. Eksp. Khim.*, 10, 508 (1974).
5. M. Simalty, H. Strzelecka, and H. Khediya, *Tetrahedron*, 27, 3503 (1971).
6. R. Sprague and L. Brooker, *J. Am. Chem. Soc.*, 59, 2697 (1937).
7. J. Wilt, G. Reynolds, and J. Van Allan, *Tetrahedron*, 29, 795 (1973).
8. B. I. Stepanov and L. P. Kazachenko, *Opt. Spektrosk.*, 12, 131 (1962).
9. G. G. Dyadyusha and A. A. Ishchenko, in: *Collection of Annotations of Programs for Molecular Spectroscopy* [in Russian], Novosibirsk (1977), p. 22.
10. S. Hunig, B. Garner, G. Ruider, and W. Schenk, *Ann.*, Nos. 5/6, 1036 (1973).
11. E. D. Sych, Zh. N. Belaya, and G. G. Dyadyusha, *Ukr. Khim. Zh.*, 30, 1065 (1964).
12. Yu. A. Kruglyak, V. S. Kvakush, G. G. Dyadyusha, and V. I. Khil'chenko, *Methods for Calculations in Quantum Chemistry. Calculation of the π -Electron Structures of Molecules by Simple Molecular Orbital Methods* [in Russian], Naukova Dumka, Kiev (1967).
13. A. Balaban and C. Nenitzescu, *Ann.*, 625, 74 (1959).

DIPOLE MOMENTS AND UV SPECTRA OF SOME TWO-RING CYCLIC SULFIDES

E. N. Kharlamova, E. N. Gur'yanova, S. K. Klimenko,
and V. G. Kharchenko

UDC 547.818:543.52'422.6

The dipole moments and UV spectra of 17 compounds of the 5,6-tetramethylene- and 5,6-trimethylenethiapyran series and their saturated analogs were measured. The dipole moments of the investigated compounds range from 1.2 to 2.0 D. The effect of the size of the saturated side ring and the position of the unsaturated bonds in the sulfur-containing heteroring on the dipole moments is demonstrated. The UV spectra of the compounds with, respectively, five- and six-membered saturated side rings are virtually identical. The position of the bands is determined primarily by the structure of the heteroring.

The structures of cyclic sulfides have been previously investigated [1-3]. In the present research we measured the dipole moments and UV spectra of a number of 5,6-tetramethylene- and 5,6-trimethylenethiapyrans and their saturated analogs (see Table 1). It seemed of interest to establish the effect of the size of the saturated side ring and the position of the unsaturated bonds in the sulfur-containing heteroring on the polar and spectral properties of the sulfides.

The dipole moments of all of the investigated compounds range from 1.2 to 2.0 D. However, these relatively small differences make it possible to establish some general principles of the effect of substituents on the polar properties of the two-ring cyclic sulfides.

First of all, one's attention is drawn to the fact that the dipole moments of the compounds with six-membered side rings (I, III, V, XI, and XIII) are ~0.2-0.3 D higher than the dipole moments of the corresponding compounds with five-membered rings (II, IV, VI, XII, and XIV). The reason for the observed differences may be the different geometries of the sulfur-containing rings in 5,6-trimethylene- and, respectively, 5,6-tetramethylene derivatives, as well as the different contributions of the side rings to the overall dipole moment of the molecule. Judging from the fact that the UV spectra of compounds with, respectively, five- and six-membered side rings are virtually identical (see Table 1), it may be concluded that the character of the electronic interaction and, evidently, the geometry of the sulfur-con-

L. Ya. Karpov Scientific-Research Physical-Chemistry Institute, Moscow 107120. N. G. Chernyshevskii Saratov State University, Saratov 410601. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 6, pp. 744-747, June, 1978. Original article submitted July 5, 1977.