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PYRYLOCYANINES. 25*

THREE-DIMENSIONAL STRUCTURES OF PYRYLO-2-MONOMETHINECYANINES AND THEIR HETEROANALOGS

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UDC 547.812.5'818.1'821.3:541.63:543.422.25

Symmetrical tetra-tert-butyl-substituted pyrylo-2- and thiopyrylo-2-monomethinecyanines were synthesized by the condensation of 2-methyl-4,6-di-tert-butylpyrylium and -thiopyrylium salts, respectively, with 2-(alkylthio)-4,6-di-tert-butylpyrylium and -thiopyrylium salts. The pyrylo-2-cyanine obtained was converted to a tetra-tert-butyl-substituted pyrido-2-monomethinecyanine by treatment with methylamine. It was shown by PMR spectroscopy that, in contrast to pyrido-2-monomethinecyanine, which exists in the E,E form, its oxygen-containing analog exists in the E,Z form, and its sulfur-containing analog exists in the Z, Z configuration.

The regularities in the absorption spectra of pyrylo-2-cyanines and their sulfur- and nitrogen-containing analogs have been studied in detail [1]. However, in the investigation of these regularities the possibility of the existence of these dyes in different stereoisomeric forms has not yet been taken into account, since, in contrast to polylmethine dyes constructed from nitrogen-containing heterocycles [2], data on the three-dimensional structures of pyrylo- and thiopyrylocyanines have not been available. Information regarding the fine chemical structures of the indicated dyes would also facilitate their purposeful synthesis for the spectral sensitization of electrophotographic materials [3] and quantum electronics [4], in which they find practical application.

In the present research we set out to use PMR spectroscopy to investigate the three-dimensional structures of symmetrical pyrylo-2-, thiopyrylo-2-, and pyrido-2-monomethinecyanines. Tetra-tert-butyl-substituted dyes were selected as the subjects of the study in view of the considerably greater ease of interpretation of their PMR spectra as compared with the spectra of their tetraphenyl-substituted analogs.

The pyrylo- and thiopyrylomonomethinecyanines were obtained by the usual method for the synthesis of monomethinecyanines — by condensation of the corresponding 2-methyl-substituted heterocyclic salts with their 2-alkylthio analogs. We have previously described 2,4-di-tert-butyl-6-methylpyrylium tetrafluoroborate (Ia) and 2,4-di-tert-butyl-6-methylthiopyrylium perchlorate (Ib) [1].

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*See [1] for Communication 24.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 167-171, February, 1988. Original article submitted September 16, 1986.

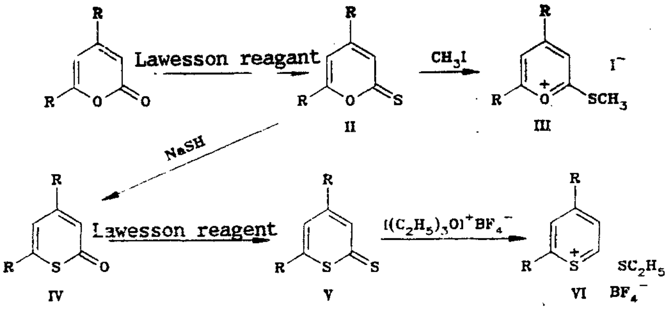
0009-3122/88/2402-0135$12.50

TABLE 1. PMR Spectra of Monomethinecyanines VIIa-c

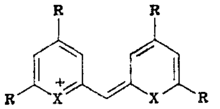
Dye	T, °C	Chemical shift, δ, ppm (J, Hz)									
		4-C(CH$_3$)$_3$ (9H, s)	4'-C(CH$_3$)$_3$ (9H s)	2-C(CH$_3$)$_3$ (9H, s)	2'-C(CH$_3$)$_3$ (9H, s)	N—CH$_3$ (6H, s)	7-H (1H, s)	3-H	3'-H	5-H	5'-H
VIIa	25	1,32 (18H, s)		1,42 (18H, s)		—	6,27	6,96 (2H, br. s)		7,49 (2H, br. s)	
	−40	1,27	1,36	1,38	1,46	—	6,29	6,91 (1H, d) [J=1,8]	7,15 (1H, d) [J=1,8]	7,19 (1H, d) [J=1,8]	7,79 (1H, d) [J=1,8]
VIIb	25	1,37 (18H, s)		1,56 (18H, s)		—	7,79	7,77 (2H, s)		7,81 (2H, s)	
	−60	1,37 (18H, s)		1,57 (18H, s)		—	7,87	7,84 (2H, s)		7,87 (2H, s)	
VIIc	25	1,25 (18H, s)		1,52 (18H, s)		3,88	5,04	6,87 (2H, d) [J=2]		7,60 (2H, d) [J=2]	
	−65	1,25 (18H, s)		1,52 (18H, s)		3,89	5,06	6,90 (2H, d) [J=1,6]		7,63 (2H, d) [J=1,6]	

Methylthiopyrylium salt III was obtained by treatment of 4,6-di-tert-butyl-2H-pyran-2-one [6] with the Lawesson reagent [5] with subsequent alkylation of the resulting thione II with methyl iodide. 2H-Thiopyran-2-one IV, which we obtained by the action of anhydrous sodium hydrosulfide on 2H-pyran-2-thione II, was converted to 2H-thiopyran-2-thione V. The latter, by the addition of Meerwein's salt, forms ethylthio derivative VI, which, immediately after preparation, was subjected to condensation with salt Ib.

The synthesis of pyrylomonomethinecyanine VIIa on the basis of salts Ia and III was carried out in pyridine, while the synthesis of thiopyrylomonomethinecyanine VIIb from Ib and VI was carried out in acetonitrile in the presence of dicyclohexylethylamine. Pyridomonomethinecyanine VIIc was obtained by treatment of dye VIIa with methylamine.



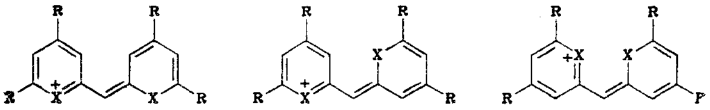
R=C(CH$_3$)$_3$



VIIa-c

VII a X=O, b X=S; c X=NCH$_3$; R=C(CH$_3$)$_3$

The three forms E,E, E,Z, and Z,Z are fundamentally possible for the cations of the type of dyes under consideration:



E, E E, Z Z, Z

It has been shown by PMR spectroscopy [2] that the E,E conformation is characteristic for unsubstituted pyrido-2-monomethinecyanine in solution. This is due to the fact that in the other two forms, if they are planar, one should observe significant steric hindrance between the methyl group attached to the nitrogen atom of one of the heterocycles and the β-hydrogen atom (the E,Z conformation) or the analogous methyl group of the second heterocycle (the Z,Z conformation). For the same reason, tetra-tert-butyl-substituted pyrido-2-monomethinecyanine VIIc should also exist in an identical E,E conformation. On the other hand, it follows from projection formulas constructed taking into account the lengths of the interatomic bonds, the bond angles, and the effective radii of the atoms [7] that the maximum steric hindrance for pyrylo- and thiopyrylomonomethinecyanines VIIa,b is observed for the E,E structure, on the basis of which one should expect that these dyes have different three-dimensional structures.

The chemical shifts of the protons in the PMR spectra of monomethinecyanines VIIa-c are presented in Table 1. An analysis of these data confirms the assumption that pyridomonomethinecyanine VIIc exists in the E,E form. In fact, in its spectrum the α-, as well as the γ-tert-butyl, groups of both heterorings show up in the form of a single signal, and only one signal is also observed for the two equivalent NCH_3 groups. The β protons also show up as two equivalent pairs. The signals of these protons have the form of two doublets. In the case of the E,Z structure one should have expected different signals for all of the indicated groups. An identical spectral pattern could also be observed in the case of the existence of VIIc in equilibrium state E,E $\rightleftarrows$ Z,Z, when they undergo rapid interconversion. However, the spectrum does not change when the temperature is decreased from 25°C to −65°C; this at least indicates that this compound exists primarily (up to 90%) in the E,E form.

The PMR spectrum of pyrylomonomethinecyanine VIIa measured over the temperature range from +40°C to −40°C is similar to the spectrum of dye VIIc at both room temperature and at elevated temperatures. However, when the temperature is lowered in this case the signals of the tert-butyl groups and the β protons become the broader and then become separate, so that four singlets of the tert-butyl groups, four doublets of the β protons, and a virtually unchanged signal of the proton of the chain are observed at −40°C. This behavior of the spectrum indicates that the pyrylomonomethinecyanine VIIa molecule and, probably, all of the pyrylo-2-monomethinecyanines, in contrast to their nitrogen analogs, exist in solution primarily in the E,Z conformation. If the E,E $\rightleftarrows$ E,Z or E,Z $\rightleftarrows$ Z,Z equilibrium did exist, the spectrum observed at low temperature would be more complex.

As in the case of the spectra of the two preceding dyes, identical character of the signals of both the α and γ-tert-butyl groups and the presence of signals of two pairs of identical β protons are characteristic for the PMR spectrum of thiopyrylomonomethinecyanine VIIb determined at 25°C. However, in this case, as in the case of pyridocyanine VIIc, the character of the spectrum does not change when the temperature is lowered to −60°C. On the basis of these data one can only conclude that the thiopyrylomonomethinecyanine VIIb molecule exists in one of the symmetrical conformations: E,E or Z,Z. An attempt to use the Overhauser nuclear effect for a definitive choice between these forms did not lead to the desired result because of the closeness of the signals of the β protons and the proton of the methine group of the chain. Nevertheless, the Z,Z structure should be considered to be more likely on the basis of the following (even though indirect) data. First, as noted above, steric hindrance is smaller for the indicated form than for the E,E form. One should then expect that the chemical shifts of the β protons and β' protons for the E,E form should differ markedly from one another. Due to deshielding by the identical proton of the second heterocyclic ring, the signals of the protons directed toward the polymethine chain should experience a significant paramagnetic shift as compared with the signal of the protons situated between the tert-butyl substituents. However, in the case of the Z,Z form the difference between the shifts of these protons should be considerably smaller. In fact, difference $\Delta\delta_{\beta'-\beta}$ is 0.73 ppm for VIIc, whereas it is only 0.04 ppm for VIIb. However, this effect cannot be ascribed entirely to the existence of examined nitrogen- and sulfur-containing dyes in different conformations. It is also affected by the fact that, because of the smaller tendency for conjugation of the sulfur atoms as compared with the nitrogen atoms in thiopyrylo-2-cyanines, the carbon—carbon bonds of the heteroresidues participate to a greater extent in the overall conjugation system than in pyrido-2-cyanines [8]. By virtue of this one should expect that the π-electron densities on the β,β'-carbon atoms of each of the heteroresidues should be closer in thiopyrylo-2-cyanine molecules. In fact, according to the results of quantum-chemical calculations by the simple Hückel MO method with the parameters in [9], the difference in effective charges $\Delta q_\beta - q_{\beta'}$ for VIIc is 0.0199, as compared with 0.0066 for VIIb.

The existence of thiopyrylomonomethinecyanine VIIb molecule in the Z,Z conformation is also in agreement with the large shift of the long-wave absorption band on passing from this dye to its higher vinylog [1], which is 212 nm for solutions in CH_2Cl_2. The analogous values in series of similar pyrylo- and pyridocyanines are 139 and 81 nm, respectively. An unusually high value of this shift (219 nm) is also observed in series of tetraphenyl-substituted thiopyrylo-2-cyanines [8]. It is known that the first vinylene shift in series of polymethine

TABLE 2. Characteristics of the Synthesized Compounds

Compound	mp,* °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	Hal	S (N)		C	H	Hal	S (N)	
II	103—104	69,9	9,0	—	14,4	$C_{13}H_{20}OS$	69,6	8,9	—	14,3	90
III	164—165	—	—	35,1	8,9	$C_{14}H_{23}IOS$	—	—	34,7	8,7	90
IV	54—56	70,1	9,0	—	14,2	$C_{13}H_{20}OS$	69,6	8,9	—	14,3	69
V	100—102	64,9	8,2	—	26,6	$C_{13}H_{20}S_2$	65,0	8,3	—	26,7	83
VIIa	178—180	64,9	8,3	7,0	—	$C_{27}H_{41}ClO_6$	65,2	8,3	7,0	—	42
VIIb	238—240	—	—	6,8	11,9	$C_{27}H_{41}ClO_4S_2$	—	—	6,7	12,1	54
VIIc	235—238	—	—	7,0	(5,6)	$C_{29}H_{47}ClN_2O_4$	—	—	6,8	(5,4)	40

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*Compound II was crystallized from hexane, IV was crystallized from petroleum ether, V was crystallized from pentane, VIIa was reprecipitated from solution in ethanol by the addition of ether, VIIb was crystallized from ethanol, and VIIc was crystallized from tert-butyl alcohol.

dyes constructed from different sulfur-containing heterocycles such as benzothiazolium, dithiolium, and other residues is 130-150 nm, i.e., it exceeds the usual value for polymethine dyes by 100 nm. This was explained by the fact that the absorption maxima of the corresponding monomethinecyanines undergo a hypsochromic shift due to exchange interaction between the nonbonded sulfur atoms of two heteroresidues [10]. Let us note that in the case that we examined the observed vinylene shift is greater than for the examples noted in [10]. This is evidently associated with the fact that the sulfur atoms that enter directly into the principal conjugation chain participate in exchange interaction in dyes of the VIIb type, while the sulfur atoms in the cases described in [10] can be regarded as substituents in the chromophore.

EXPERIMENTAL

The PMR spectra of II-V were determined with a Tesla BS-467 spectrometer (60 MHz) relative to hexamethyldisiloxane (HMDS) (II in CCl_4, and III-V in $CDCl_3$); the PMR spectra of solutions of VIIa-c in $(CD_3)_2CO$ were recorded with a Bruker WP-200 spectrometer. The electronic spectra of solutions in CH_2Cl_2 stabilized with 1% absolute ethanol were measured with an SF-8 spectrophotometer. The purity of the preparations was monitored by TLC on Silufol UV-254 plates with acetonitrile as the eluent.

4,6-Di-tert-butyl-2H-pyran-2-thione (II, Table 2). A mixture of 1.04 g (5 mmole) of 4,6-di-tert-butyl-2H-pyran-2-one [6] and 1.212 g (3 mmole) of the Lawesson reagent [5] in 10 ml of dry toluene was heated in an argon atmosphere for 1 h at 110°C. The product was purified by chromatography on Al_2O_3 with chloroform as the eluent. UV spectrum, γ_{max} (log ε): 279 (3.90), 377 nm (4.05). PMR spectrum, δ: 1.19 [9H, s, γ-$C(CH_3)_3$], 1.30 [9H, s, α-$C(CH_3)_3$], 6.12 (1H, d, J = 2 Hz, β-H), 6.80 ppm (1H, d, J = 2 Hz, β'-H).

2,4-Di-tert-butyl-6-(methylthio)pyrylium Iodide (III). A mixture of 0.485 g (2.2 mmole) of thione II and 4 g (28 mmole) of methyl iodide in 8 ml of dry benzene was heated for 1 h at 90°C, after which the salt was removed by filtration and washed with dry benzene and ether. UV spectrum, γ_{max} (log ε): 357 nm (4.17). PMR spectrum, δ: 1.36 [9H, s, γ-$C(CH_3)_3$], 1.47 [9H, s, α-$C(CH_3)_3$], 2.96 (3H, s, SCH_3), 7.30 (1H, d, J = 2 Hz, β-H), 7.88 ppm (1H, d, J = 2 Hz, β'-H).

4,6-Di-tert-butyl-2H-thiopyran-2-one (IV). A solution of 1.6 g (29 mmole) of anhydrous sodium hydrosulfide in 30 ml of dry hexamethylphosphoric triamide was added with stirring to a solution of 1.82 g (8 mmole) of thione II in 30 ml of dry THF, and the mixture was heated at 80°C for 1.5 h; 30 ml of absolute methanol was then added, and the mixture was heated for another hour. It was then cooled and treated with 40 ml of ether and 50 ml of water. The organic layer was separated, the aqueous layer was extracted with ether, and the solvent was evaporated. UV spectrum, γ_{max} (log ε): 331 nm (3.71). PMR spectrum, δ: 1.19 [9H, s, γ-$C(CH_3)_3$], 1.27 [9H, s, α-$C(CH_3)_3$], 6.26 (1H, s, β-H), 6.74 ppm (1H, s, β'-H).

4,6-Di-tert-butyl-2H-thiopyran-2-thione (V). This compound was obtained from IV by a procedure similar to that used to prepare II. UV spectrum, γ_{max} (log ε): 250 (4.06), 315 (3.85), 436 nm (3.72). PMR spectrum, δ: 1.24 [9H, s, γ-$C(CH_3)_3$], 1.32 [9H, s, α-$C(CH_3)_3$], 7.05 (1H, s, β-H), 7.42 ppm (1H, s, β'-H).

2-[(4,6-Di-tert-butyl-2-pyranylidene)methyl]-4,6-di-tert-butylpyrylium Perchlorate (VIIa). A mixture of 0.294 g (1 mmole) of salt Ia and 0.366 g (1 mmole) of salt III in 4 ml of dry pyridine was heated at 110°C for 1 h, after which it was cooled and treated with excess 20% $HClO_4$. The product was purified by reprecipitation from ethanol with an aqueous solution of sodium perchlorate and then from ethanol by the addition of ether. UV spectrum γ_{max} (log ε): 286 (3.87), 302 (3.83), 314 (3.92), 496 (4.63), 529 nm (4.79).

2-[(4,6-Di-tert-butyl-2-thiopyranylidene)methyl]-4,6-di-tert-butylthiopyrylium Perchlorate (VIIb). A solution of 0.190 g (1 mmole) of Meerwein's salt in 1.5 ml of methylene chloride was added to a mixture of 0.240 g (1 mmole) of thione V in 1.5 ml of methylene chloride, and the mixture was allowed to stand overnight at room temperature. The solvent was evaporated in vacuo, 0.322 g (1 mmole) of salt Ib in 5 ml of acetonitrile and 0.210 g (1 mmole) of dicyclohexylethylamine were added, and the mixture was heated for 2 h at 90°C. The mixture was then cooled and poured into 100 ml of 10% perchloric acid, and the dye was removed by filtration and washed with water, ethanol, and ether. UV spectrum, γ_{max} (log ε): 286 (4.05), 348 (3.65), 400 (3.51), 570 nm (4.79).

1-Methyl-2-[(1-methyl-4,6-di-tert-butyl-1,4-dihydro-2-pyridinylidene)methyl]-4,6-di-tert-butylpyridinium Perchlorate (VIIc). A mixture of 0.165 g (0.33 mmole) of pyrylocyanine VIIa and 1 ml (3.3 mmole) of a 10% methanol solution of methylamine in 3 ml of DMF was heated at 100°C for 5 h, after which it was cooled, and the dye was precipitated with an aqueous solution of sodium perchlorate. UV spectrum, γ_{max} (log ε): 266 (3.68), 360 (3.64), 494 nm (4.66).

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