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CARBOCYANINE DYES WITH AN o-HYDROXYARYL SUBSTITUENT IN THE MESO POSITION OF THE POLYMETHINE CHAIN

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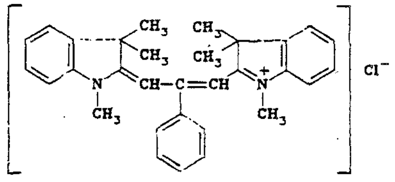
Carbocyanine dyes with an o-hydroxyaryl substituent in the meso position of the polymethine chain were obtained from o-hydroxybenzoyl derivatives of the Fischer base and heterocyclic methylene bases (1,3,3-trimethyl-2-methyleneindoline, 1-ethyl-4-methylene-1,4-dihydroquinoline, and 1-methyl-2-methylene-1,2-dihydroquinoline) in the presence of phosphorus oxychloride. The symmetrical indolenine dyes exist in the colorless spiropyran form in an alkaline medium. The unsymmetrical carbocyanines with a quinoline fragment do not form a spiro form and are deeply colored compounds; this is explained by their open dipolar structure.

Compounds that have the properties of sensitizers have been found among carbocyanine dyes that contain an aryl substituent in the polymethine chain [1, 2]. The simplest indolenine carbocyanine with a meso-phenyl substituent (I) was obtained by heating the benzoyl



I

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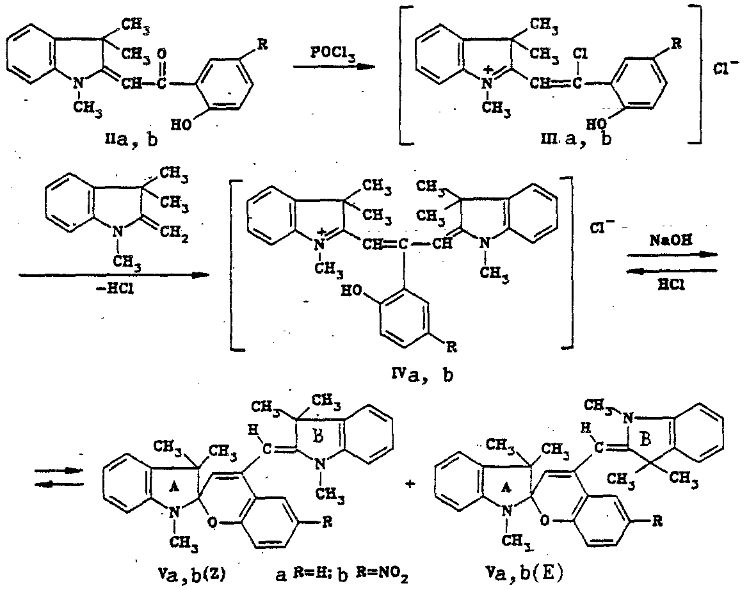
derivative of the Fischer base with phosphorus oxychloride and the subsequent action of 1,3,3-trimethyl-2-methyleneindoline [1].

In the present research we studied the reaction of o-hydroxyaroyl derivatives (II) of the Fischer base with various heterocyclic methylene bases under the same conditions in order to obtain carbocyanine dyes that contain an o-hydroxyaryl substituent in the meso position. Similar dyes, which are known in the benzothiazole series, were obtained by cleavage of the pyrylium ring of pyrylocyanines [3, 4]. According to the data in [5], they are converted by the action of alkali to colorless anhydro bases, which have a spiropyran form. We established that enamino hydroxy ketones II, which are readily obtained by acylation of the Fischer base with O-acetylsalicylic acid chlorides [6], react in the form of indoleninium salt III [7] with 1,3,3-trimethyl-2-methyleneindoline to give carbocyanine dyes IV, which undergo spirocyclization under the influence of alkali.

Spiropyrans V are slightly yellow compounds, solutions of which take on a deep violet color only when acids (hydrochloric, acetic) are added; this is associated with opening of the pyran ring and the formation of dye IV. The compositions and structures of spiropyrans V were confirmed by the results of elemental analysis and PMR spectral data. Analysis of the latter showed that V are produced in the form of mixtures of E and Z stereoisomers in a ratio of 1:1. The chemical shifts of the most characteristic protons are presented in Table 1. For the spiroindoline fragment (A) they are in good agreement with the PMR spectra of known spirobenzopyrans [8], while for the methyleneindoline fragment (B) they are in good agreement with the analogous spectrum of the Fischer base [9]. The assignment of the signals to E and Z configurations was made from the chemical shifts of the protons that are most sensitive to steric changes in the structure. Thus in the Z configuration the signal of the protons of the N–CH_3 group of the B ring is shifted to weak field (anisotropy of the closely located benzopyran fragment), while the 4-CH signal is shifted to strong field (separation from the heteroarom of the CH_3N group).



The data presented in Table 1 provide evidence that the PMR spectrum of spiro compound Vb in a polar solvent – deutero-dimethyl sulfoxide – is virtually the same as the spectrum of Vb in deuterated chloroform. This fact indicates high stability of the spiro form of the carbocyanine dye even in the presence of a nitro group, which usually facilitates conversion to the open structure. According to the data in [5], the spirocyclic anhydro bases of thiacyanine dyes are unstable compounds: their spiropyran rings open up under the influence of a polar solvent, and they rapidly take on a blue coloration in air. With respect to their structures, spiro compounds V differ from the thia analogs with respect to the presence in the 3' position of two methyl groups, which, in combination with the bulky methyleneindoline substituent in the 4 position, evidently create steric hindrance to opening of the pyran ring.

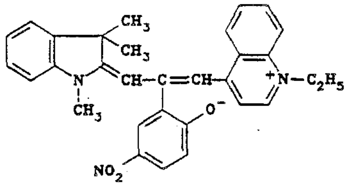
Spiro compounds V are formed from symmetrical carbocyanine dyes IV, as a consequence of which the formation of a pyran ring at one or the other indoline fragment is equally likely and indistinguishable. It therefore was of interest to accomplish the synthesis of unsymmetrical carbocyanine dyes and to ascertain the heteroring at which the formation of their spiro form would occur. For this, substituted indoleninium salt IIIb was treated with the

TABLE 1. PMR Spectra of the Geometrical Isomers of Spiropyrans V [in $(CD_3)_2SO$]

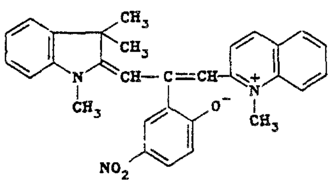
Compound	Configuration	Chemical shifts, δ, ppm						
		Heteroring A		Heteroring B		3-H	4-CH	Aromatic protons
		$C(CH_3)_2$	$N—CH_3$	$C(CH_3)_2$	$N—CH_3$			
Va	Z	1,31; 1,18	2,71	1,44; 1,42	3,15	5,14	5,56	6,54—7,34 (12H)
	E	1,27; 1,14	2,68	1,44; 1,44	3,08	5,19	5,69	
Vb	Z	1,31; 1,21	2,74	1,40; 1,48	3,20	5,21	5,73	6,60—8,19 (11H)
	E	1,27; 1,18	2,69	1,48; 1,48	3,08	5,23	5,91	
Vb	Z*	1,37; 1,27	2,79	1,47; 1,52	3,21	5,02	5,71	6,54—8,26 (11H)
	E*	1,33; 1,24	2,74	1,52; 1,52	3,13	5,05	5,88	

*In $CDCl_3$.

methylene bases obtained from the quaternary salts of lepidine and quinaldine. However, in this case, instead of the expected spiropyrans of the V type, we obtained unsymmetrical carbocyanine dyes VI and VII, which, despite the presence of an o-hydroxyphenyl substituent in the polymethine chain, exist in a dipolar colored form. This is possibly explained by the fact that this open structure is thermodynamically more stable, since the formation of a pyran ring at either heteroring leads to disruption of the aromatic character of the pyridine ring.

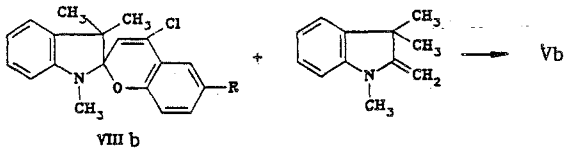


VI



VII

The yields of Va, b, VI, and VII are low (21%, 44%, 16%, and 4%, respectively). In the case of the synthesis of VI and VII we were able to isolate small amounts of 4-chloro-substituted spiropyrans VIIIa, b (R = H and R = NO_2) from the reaction mixtures (see the experimental section). Spiropyran Vb was obtained in high yield (90%) by heating a mixture of VIIIb and the Fischer base in the presence of triethylamine.



Spiro compounds V were tested as chromogenic components for heat-sensitive coatings. It was established that at 130°C they give contrast printings, but the latter are unstable with respect to light. Unsymmetrical carbocyanine dyes VI and VII were tested as components of polymeric detectors of ionizing radiation. The tests showed that these dyes increase the selectivity of etching, which leads to the formation of distinct tracks left by α particles; however, a higher concentration of the dye in the polymer layer cannot be created because of the low solubility in the solvents used (acetone, butyl acetate).

EXPERIMENTAL

The PMR spectra were recorded with a high-resolution spectrometer with a WP-200SY superconducting magnet (200 MHz). Silica gel L 40/100 was used for column chromatography. The R_f values were determined on Silufol UV-254 plates with chloroform as the eluent.

1',3',3'-Trimethyl-4-(1,3,3-trimethyl-2-indolinylidenemethyl)spiro(2H-1-benzopyran-2,2'-indoline) (Va). A mixture of 2.93 g (10 mmole) of enamino hydroxy ketone IIa [6] and 2.28 g (15 mmole) of phosphorus oxychloride was refluxed for 4 h in 50 ml of 1,2-dichloroethane, after which the mixture was cooled to room temperature, 3.44 g (20 mmole) of the Fischer base in 10 ml of 1,2-dichloroethane was added, and the resulting mixture was refluxed for another hour. It was then poured into 200 ml of cold water, and the aqueous mixture was neutralized to pH 7-8 with aqueous NaOH solution. The organic layer was separated and dried with sodium sulfate, and the solvent was evaporated. The residue was chromatographed on a column. Initial elution with benzene–hexane (1:1) gave 0.15 g of 4-chlorospiropyran VIIIa (R = H) with R_f 0.74 and mp 127-129°C [6]; the yield was 5% based on IIa. Subsequent elution with benzene gave spiro compound Va, with R_f 0.49, in 21% yield; crystallization from ethanol gave colorless crystals with mp 91-92°C. Found: C 83.3; H 7.0; N 6.5%. $C_{31}H_{32}N_2O$. Calculated: C 83.0; H 7.2; N 6.2%.

1',3',3'-Trimethyl-4-(1,3,3-trimethyl)-2-indolinylidenemethyl)-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) (Vb). A. This compound was synthesized from 3.34 g (10 mmole) of enamino hydroxy ketone IIb [6] by a method similar to that used to obtain Va. Elution with benzene—petroleum ether (bp 40-70°C) (2:1) gave 0.15 g (4.1%) of spiropyran VIIIb (R = NO_2) with R_f 0.62 and mp 170-173°C [6]. Subsequent elution with benzene gave 2.19 g (44%) of a substance with R_f 0.41; crystallization from ethanol gave yellow crystals with mp 198-200°C. Found: C 75.7; H 6.4; N 8.6%. $C_{31}H_{31}N_3O_3$. Calculated: C 75.5; H 6.3; N 8.5%.

B. A mixture of 0.21 g (0.6 mmole) of spiropyran VIIIb (R = NO_2) [6], 0.12 g (0.7 mmole) of the Fischer base, and 0.07 g (0.7 mmole) of triethylamine in 15 ml of chloroform was refluxed for 3 h, after which it was allowed to stand overnight at room temperature and then refluxed for another hour. The reaction mixture was washed successively with 0.5% hydrochloric acid solution and water and dried with sodium sulfate. The chloroform was evaporated to give 0.27 g (90%) of a crystalline substance with mp 186-190°C and R_f 0.41; crystallization from ethanol gave yellow crystals with mp 198-200°C.

1-(1-Ethyl-4-quinolinia)-2-(2-oxido-4-nitrophenyl)-3-(1,3,3-trimethyl-2-indolinylidene)-propene (VI). A mixture of 1.14 g (5 mmole) of enamino hydroxy ketone IIb and 1.14 g (7.5 mmole) of phosphorus oxychloride in 30 ml of dichloroethane was heated at 80°C for 5 h, after which a solution of 1-ethyl-4-methylene-1,4-dihydroquinoline in dichloroethane was added. [The solution of the latter compound was prepared by adding 8 ml of 10% NaOH solution to 2.99 g (10 mmole) of 1-ethyl-4-methylquinolinium iodide in 15 ml of water; the resulting precipitate was extracted with 50 ml of dichloroethane, and the solution was dried with sodium sulfate and filtered]. The mixture was refluxed for 4 h, after which it was poured into 100 ml of cold water. The aqueous mixture was neutralized with 10% NaOH solution, and the organic layer was separated and dried with sodium sulfate. The solvent was evaporated, and the residue was chromatographed with methylene chloride—ether (20:1) to give 0.4 g (16%) of a substance with R_f 0.42 and mp 270-280°C; crystallization from ethanol gave dark-violet crystals with mp 290-294°C. PMR spectrum ($CDCl_3$): 1.00; 1.50 [6H, two s, $C(CH_3)_2$]; 3.17 (3H, s, $N-CH_3$); 1.34 (3H, t, CH_3CH_2); 4.00 (2H, q, $\overset{+}{N}-CH_2$, $J_{CH_3CH_2}$ = 7.9 Hz); 6.45-8.85 ppm (15H, m, remaining protons). Found: C 75.9; H 6.1; N 8.4%. $C_{31}H_{29}N_3O_3$. Calculated: C 75.7; H 5.9; N 8.6%.

1-(1-Methyl-2-quinolinia)-2-(2-oxido-4-nitrophenyl)-3-(1,3,3-trimethyl-2-indolinylidene)-propene (VII). This compound was synthesized from 1.7 g (5 mmole) of enamino hydroxy ketone IIb, 1.14 g (7.5 mmole) of phosphorus oxychloride, and 2.85 g (10 mmole) of quinaldine methiodide in 60 ml of dichloroethane by a method similar to that used to obtain carbocyanine VI. This procedure gave 0.1 g (4%) of a dark-violet substance with R_f 0.62 and mp 265-269°C. PMR spectrum ($CDCl_3$): 1.06; 1.57 [6H, two s, $C(CH_3)_2$]; 3.15 (3H, s, $N-CH_3$); 3.57 (3H, s, $\overset{+}{N}-CH_3$); 6.48-8.76 ppm (15 H, m, remaining protons). Found: C 75.8; H 5.6; N 8.5%. $C_{30}H_{27}N_3O_3$. Calculated: C 75.5; H 5.7; N 8.8%.

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