

POLYMETHINE DYES BASED ON (BENZO-15-CROWN-5)THIAZOLE

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Several monomethinecyanine, merocyanine and styryl dyes were synthesized using a 5,6-(1,4,7,10,13-pentaoxacyclotridecane)-benzothiazole derivative as the starting reagent. A study was made of their spectral characteristics and the effect which complexing with alkaline and alkaline-earth metal salts had on their chromaticity.

Over recent years there has been an upsurge in research into polyfunctional compounds containing both macroheterocyclic moieties and organic dyes or luminophores capable of changing their spectral properties in the course of "guest-host" type complex formation [1, 2]. Azo dyes are the most widely studied in this respect, but their absorption characteristics are not highly selective. Data on polymethine dye containing macroheterocyclic moieties is much less common. Certain styryl dyes with an aza-15-crown-5 substituent have been synthesized and investigated in a fundamental work on the subject [2], and individual studies were subsequently devoted to derivatives of this type [3]. The synthesis and analysis of styryl dyes containing benzothiazole and benzo-15-crown-5 moieties have been covered in a series of works by Russian authors. They obtained some interesting results on physicochemical properties, including photoisomerization and aggregation, by making relatively simple modifications in the base structures [4-7].

2-Methyl-5,6-(15-crown-5)benzothiazole (III) and the trimethinecyanine dyes based on it (symmetrical and asymmetrical, with an unsubstituted benzothiazole central portion) were synthesized for the purpose of using them as sensitizers in photographic materials [8, 9]. No effects on the absorption bands of this type of dye were discovered on addition of alkaline or alkaline-earth metal salts.

The ionochromic nature of polymethine dyes based on (15-crown-5)benzothiazole should be more clearly seen (as should the influence of any group in the heterocyclic moiety of dyes in general) in the case of compounds having an asymmetrical structure and a short chromophore. The aim of the present work is to investigate the synthesis and spectral characteristics of such dyes.

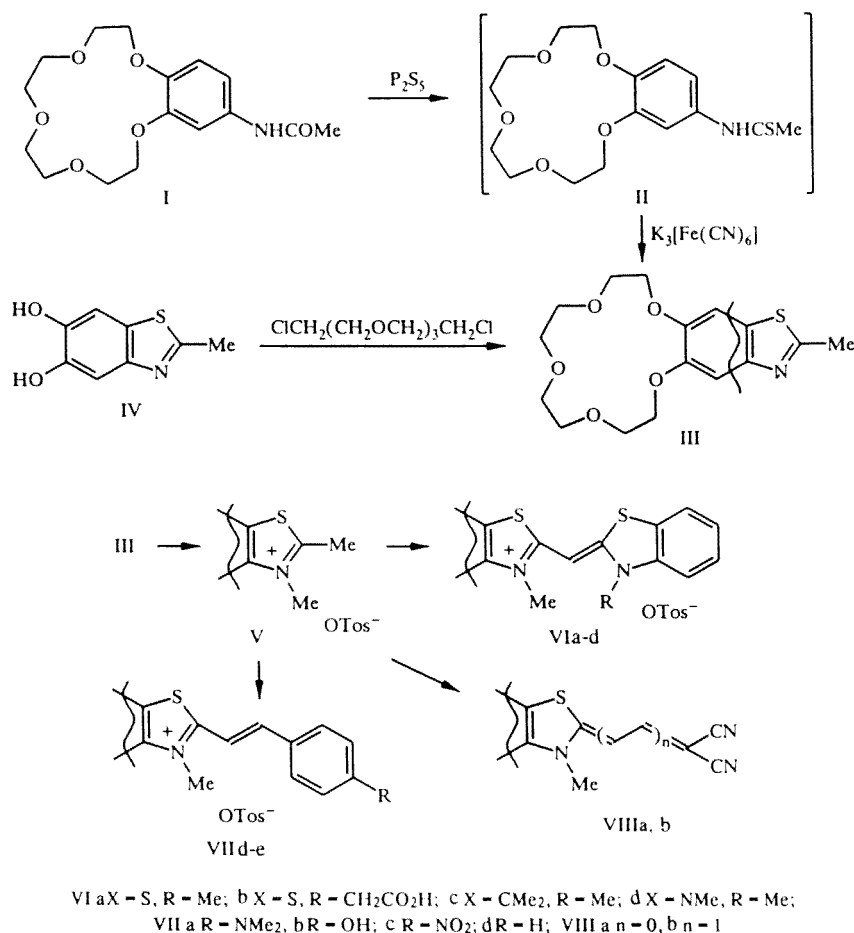
Two methodological approaches, differing from that cited in report [8], were employed to obtain benzothiazole III, used as the initial synthesis reagent. The first approach adopted the classical benzothiazole synthesis method [10], that is, replacement of the oxygen atom by sulfur in 4-acetylaminobenzo-15-crown-5, then ring closure with potassium ferrocyanide. In the second case benzothiazole III was obtained by completing the macrocyclic part, using 5,6-dihydroxy-2-methylbenzothiazole IV as the starting reagent [11]. The latter approach was considered preferable as a preparative technique.

Salt V, which was obtained by methylating base III with methyl p-toluenesulfonate, readily condensed with those electrophilic reagents which are normally used to synthesize polymethine dyes. So, for example, when boiled for a short time in acetic anhydride or pyridine, salt V reacted with substituted benzaldehydes to give styryls VIIa-e; with substituted 2-methylthiobenzothiazole salts and malonodinitrile derivatives in alcohol, the salt reacted in the presence of triethylamine to afford the corresponding monomethine-cyanines VII. Physicochemical properties of the synthesized compounds are shown in Table 1.

To study the effects of complex formation on spectral properties, absorption spectra were recorded for styryl VIIa in acetonitrile in the presence of alkaline and alkaline-earth metal salts (Table 2).

TABLE 1. Physicochemical Properties of Synthesized Compounds

Compound	mp, °C	λ_{\max} (lg ϵ)	Empirical formula	Yield, %
III	75...76, 74...75 [8]		C ₁₆ H ₂₁ NO ₅ S	23 (A), 25 (B)
V	205...206		C ₂₄ H ₃₁ NO ₈ S ₂	82
VIa	222...223	441 (4,83)	C ₃₂ H ₃₆ N ₂ O ₈ S ₃	55
VIb	153...155	441 (4,26)	C ₃₃ H ₃₆ N ₂ O ₁₀ S ₃	46
VIc	120...121	445 (4,39)	C ₂₈ H ₃₅ ClN ₂ SO ₉	54
Vd	190...192	404 (3,85)	C ₃₃ H ₃₉ N ₃ O ₈ S ₂	13
VIIa	284...285	516 (5,01)	C ₃₃ H ₄₀ N ₂ O ₈ S ₂	68
VIIb	195...197	431 (3,92)	C ₃₁ H ₃₅ NO ₃ S ₂	58
VIIc	135...137	426 (4,13)	C ₃₁ H ₃₄ N ₂ O ₁₀ S ₂	82
VIIId	117...119	426	C ₃₂ H ₃₇ NO ₉ S ₂	29
VIIe	104...105	408	C ₃₁ H ₃₅ NO ₈ S ₂	30
VIIIa	249...250	471 (4,86)	C ₂₁ H ₂₃ N ₃ O ₅ S	72
VIIIb	263...265	560 (5,18)	C ₂₃ H ₂₅ N ₃ O ₅ S	63



As the results indicate, the biggest changes in the spectra, namely the bathochromic and hyperchromic absorption band shifts, were caused by the alkaline-earth metal salts, although benzo-15-crown complexes with alkaline metal cations are more stable [1]. The effect which the metal cations had on the color of the test compounds stemmed primarily from the redistribution of electron density on the oxygen atoms bonded to the benzene ring. So, if the complexes formed between the dyes and the different salts have similar stabilities, it is the Coulomb factors which assume the greater importance, rather than the hypothetical "non-specific interactions" put forward in communication [3].

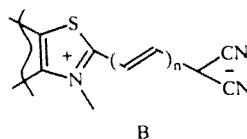
TABLE 2. Effect of Alkaline and Alkaline-Earth Metal Salts ($C = 5 \cdot 10^{-3}$ moles/liter) on Absorption Maximum of Styryl VIIa in Acetonitrile ($C = 1 \cdot 10^{-5}$ moles/liter)

	Mg(ClO ₄) ₂	Ca(ClO ₄) ₂	Ba(ClO ₄) ₂	LiClO ₄	NaClO ₄	KSCN
λ_{\max} , nm	529	529	524	519	522	518
$\Delta\lambda_{\max}$, nm	13	13	8	3	6	2

TABLE 3. Effect of Magnesium Perchlorate on Absorption Spectrum of Styryl VIIa in Acetonitrile ($C = 1 \cdot 10^{-5}$ moles/liter)

$C[Mg(ClO_4)_2]$, moles/liter	λ_{\max} , nm	$\Delta\lambda_{\max}$, nm	lg ϵ
0	516	—	5,007
$1 \cdot 10^{-5}$	517	1	5,008
$1 \cdot 10^{-4}$	520	4	5,010
$1 \cdot 10^{-3}$	526	10	5,039
$3 \cdot 10^{-3}$	528	12	5,040
$4 \cdot 10^{-3}$	529	13	5,041
$5 \cdot 10^{-3}$	529	13	5,045
$1 \cdot 10^{-2}$	529	13	5,050

Results obtained from titrating a styryl VIIa solution with magnesium perchlorate solution (Table 3) indicated that with a low-stability complex the effect reached its maximum point for a molar ratio of approximately 1:500. We adhered to this ratio in subsequent measurements. Like the other salts, magnesium perchlorate produced the opposite effect on solutions of styryls VIIb-e, monomethinecyanines VIa-d and merocyanines VIIIa and VIIIb, resulting in a hypsochromic shift (Table 4). As was mentioned above, in the course of complex formation the metal cation attracts the free electron pair from the oxygen atoms. This reduces the electron-donor capacity of these atoms and, consequently, that of the (benzo-15-crown-5)thiazole center as a whole. It is probably this factor above all others which underlies the observed spectral effects. Thus, in a VIIa-type molecule comprising dimethylaminostyryl and a benzothiazole portion a much bigger positive charge is known to be concentrated on the benzothiazole moiety than on the dimethylamino group. In the course of complexing the electron symmetry of the dye increases, resulting in an absorption band bathochromic shift. Because of the high electron-donor capacity of their malonodinitrile moiety (63°, [12]) the electron configuration of the type-VIII merocyanines approximates to a non-polar structure, and the contribution of the "B"-type structure is small. And indeed, complex formation at the crown-ether moiety reduces this contribution even further, thus explaining the observed hypsochromic effect.



The hypsochromic effect seen in monomethinecyanine VIId is also in line with the increased electron asymmetry occurring in complex formation. However, the hypsochromic effects observed in the course of complex formation in the monomethinecyanines VIa-c and styryls VIIb-e cannot be explained solely in terms of the effect which complexing has on dye electron symmetry. A clearer idea about the nature of the observed phenomena can only be obtained through further research.

EXPERIMENTAL

Absorption spectra were recorded on a Specord M-400 spectrophotometer and PMR spectra on a Bruker WP-200 instrument at 25°C, internal standard TMS.

The compounds were crystallized from the following solvents: petroleum ether (III), iso-propanol (V, VIa-c and VIIc), methanol (VIId), ethanol (VIIa, VIIb), acetonitrile (VIIIa), acetic anhydride (VIIIb).

TABLE 4. Effect of Magnesium Chlorate ($C = 5 \cdot 10^{-3}$ moles/liter) on Absorption Spectrum of Dyes VI-VIII ($C = 1 \cdot 10^{-5}$ moles/liter)

	vIa	vIb	vIc	VI d	vIIb	vIIc	vII d	vIIe	vIIIa	vIII b
λ_{\max} , nm	432	432	441	392	423	404	412	400	456	550
$\Delta\lambda_{\max}$, nm	-9	-9	-4	-12	-8	-22	-14	-8	-8	-4

TABLE 5. Elemental Analysis Data for Synthesized Compounds

Compound	Found, %		Calculated, %	
	N	S	N	S
III	4.28	9.67	4.13	9.45
V	2.84	12.42	2.66	12.20
VIa	4.33	14.48	4.16	14.30
VIb	3.84	13.45	3.91	13.42
VIc	4.42	5.01	4.59	5.24
VI d	6.09	9.45	6.28	9.57
VIIa	4.35	9.66	4.27	9.76
VIIb	2.46	10.31	2.22	10.18
VIIc	3.88	9.72	4.26	9.75
VII d	2.39	10.02	2.21	10.11
VIIe	2.42	10.24	2.28	10.42
VIIIa	9.67	7.98	9.78	7.47
VIII b	8.32	7.31	9.22	7.04

2-Methyl-5,6-(1,4,7,10,13-pentaoxacyclotridecane)thiazole (III). A. A solution of 25 g (0.077 moles) 4-acetylaminobenzo-15-crown-5 and 10 g (0.045 moles) phosphorus pentasulphide in 150 ml absolute dioxane was heated with stirring for 2.5 h at 55-60°C. When insoluble impurities had been filtered off, the solution was evaporated to dryness in vacuum and dissolved in 150 ml of a 4% caustic soda solution. The resultant solution was filtered, acidified with acetic acid until a neutral reaction was obtained, then extracted with chloroform. The organic layer was dried with magnesium sulfate and evaporated to dryness. When the oil residue (raw material II, 12 g) had been dissolved in 240 ml of 10% caustic soda, 103 g (0.313 moles) of potassium ferrocyanide in 450 ml water was added to it, the temperature being kept at 5°C or less. The mixture was stirred for a further 3 h at room temperature and extracted with methylene chloride. Then the organic layer was dried with magnesium sulphate, evaporated to dryness and recrystallized. PMR spectrum, CD₃CN: 2.82 (3H, s, CH₃); 3.70 (8H, s, 4CH₂O); 3.89 (4H, m, 2CH₂O); 4.17 (4H, m, 2CH₂O); 7.42 (1H, s, 4-H); 7.47 ppm (1H, s, 7-H).

B. A mixture of 1 g (5.54 mmoles) 2-methyl-5,6-dihydroxybenzothiazole (IV), 1.28 g (5.54 mmoles) 1,11-dichloro-3,6,9-trioxa-undecane and 2.8 g (20 mmoles) calcined potash in 15 ml DMF was stirred in an argon flow for 12 h at 100°C. After dilution with water and extraction with methylene chloride, compound III was isolated as above. PMR, elemental analysis and melting point data indicated that the substance was analogous to that obtained using method A.

2,3-Dimethyl-5,6-(1,4,7,10,13-pentaoxacyclodecane)benzothiazolium p-Toluenesulfonate (V). A mixture of 2.5 g (7.3 mmoles) benzothiazole III and 1.4 g (7.5 mmoles) methyl p-toluenesulfonate was heated for 1 h at 100°C. The melt was triturated with propanol-2, and the precipitate was filtered off. PMR spectrum, CD₃COD: 2.35 (3H, s, Tos-CH₃); 3.08 (3H, s, 2-CH₃); 3.73 (8H, s, 4CH₂O); 3.92 (4H, m, 2CH₂O); 4.18 (3H, s, N-CH₃); 4.29 (4H, 2CH₂O); 7.20 (2H, d, β-Tos-H, $J_{\alpha,\beta} = 7.2$ Hz); 7.63 (2H, α-Tos-H, $J_{\alpha,\beta} = 7.2$ Hz); 7.69 ppm (2H, s, 4-, 7-H).

3-Methyl-5,6-(1,4,7,10,13-pentaoxacyclodecane)-2-[(3-methyl-2(3H)-benzothiazolylidene)methyl]benzothiazolium p-Toluenesulfonate (VIa). A solution of 0.52 g (1 mmole) of salt and 0.37 g (1 mmole) 3-methyl-2-methylthiobenzothiazolium p-toluenesulfonate in 50 ml ethanol was brought to boiling point, then 0.11 g (1.1 mmoles) triethylamine was added to it. After cooling, the precipitate was filtered off and recrystallized.

Monomethinecyanines VIb-d were obtained in the same way from the corresponding salts.

Merocyanines VIIIa and VIIIb were obtained in the same way from 1-ethoxy-2,2-dicyanoethylene and 1-ethoxy-4,4-dicyanobutadiene-1,3 respectively.

3-Methyl-5,6-(1,4,7,10,13-pentaoxacyclodecane)-2-(p-dimethylaminostyryl)benzothiazolium p-Toluenesulfonate (VIIa). A mixture of 0.26 g (0.5 mmoles) salt V and 0.08 g (0.53 mmoles) p-dimethylaminobenzaldehyde was boiled in 5 ml pyridine for 5 min. After cooling, the dye was precipitated by adding 25 ml ether.

Styryls VIIb-e were obtained in the same way from the corresponding aldehydes.

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