

Spectroscopic investigations on derivatives of tetrahydrofuran. III.*

Carbocyanine dyes *meso*-substituted with tetrahydrofurfuryl group

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A series of compounds has been prepared in order to investigate the effect of the tetrahydrofurfuryl group attached to the α -position of dimethinemerocyanines upon the shift of the absorption maxima corresponding to the weakly pronounced electron effect ($\sigma^+ = 0.4$). It is showed that the electron effect studied is more pronounced than that of the substances having the tetrahydrofurfuryl group located in the *meso*-position of *sym*- and *asym*-thia- and -selenacarbocyanine dyes.

By the use of tetrahydrofurylacetyl chloride (*I*) [1] and the general procedure of Brooker *et al.* [2–4] a series of *meso*-tetrahydrofurfurylcarbocyanine dyes and α -tetrahydrofurfuryl substituted dimethinemerocyanines was synthesized. The aim of the work was to study the effect of the tetrahydrofurfuryl group upon the basic chromophoric system of the described types of dyes.

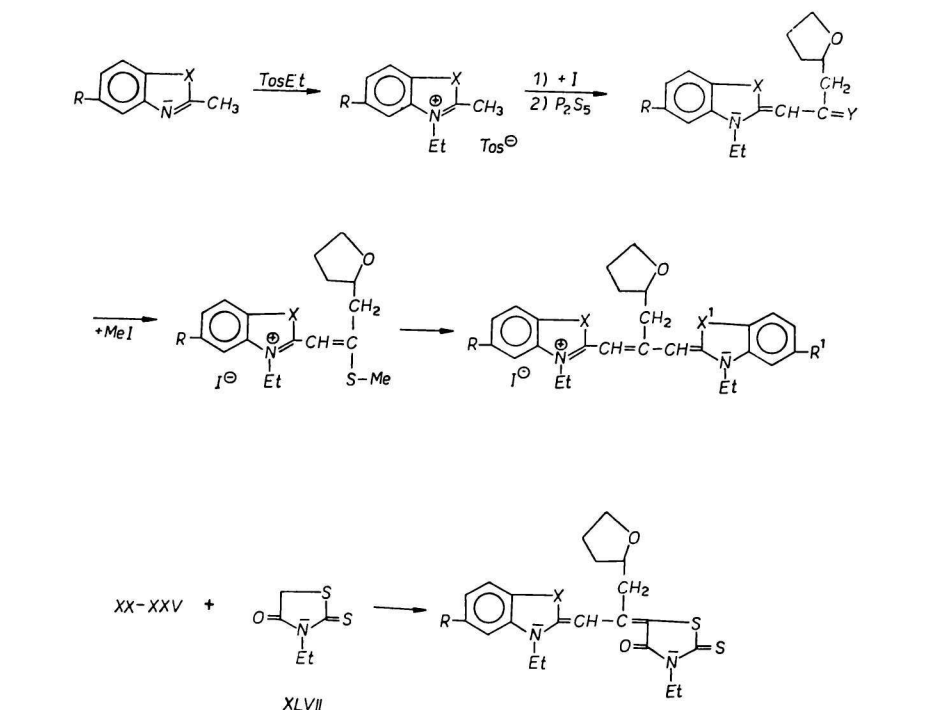
The thioacetonylidene compounds (*XIV–XIX*) were prepared by treatment of *N*-ethyl-2-(tetrahydrofurylacetonilydene)-5-*R*-benzthiazoles or -benzselenazoles (*VIII–XIII*) with phosphorus pentasulfide. *S*-Methylation with methyl iodide or dimethyl sulfate gave quaternary salts of the 2-(β -methylmercapto- β -tetrahydrofurfuryl)vinyl-*N*-ethyl-5-*R*-benzthiazolium or -benzselenazolium iodide (*XX–XXV*) type. These were allowed to react with the starting, or quaternary salt to give *meso*-tetrahydrofurfurylcarbocyanine dyes (*XXVI–XLVII*). Reaction with 3-ethylrhodanine (*XLVIII*) afforded dimethinemerocyanine dyes (*XLVIII–LIII*) (Scheme 1).

Experimental

The i.r. spectra were measured in KBr pellets or in Nujol using UR-10 (Zeiss, Jena) spectrophotometer. Other spectra, including the absorption reflexion spectra were obtained with SF-10 registration spectrophotometer (USSR). Characteristics of the synthesized compounds (products described as oils did not crystallize even after purification by chromatography), numbered as can be seen in Scheme 1, are summarized in Table 1. Some absorption data are in Table 2.

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Scheme 1

	R	X		R	X	Y
II	H	S	VIII	H	S	O
III	Me	S	IX	Me	S	O
IV	OMe	S	X	OMe	S	O
V	H	Se	XI	H	Se	O
VI	Me	Se	XII	Me	Se	O
VII	OMe	Se	XIII	OMe	Se	O
			XIV	H	S	S
			XV	Me	S	S
			XVI	OMe	S	S
			XVII	H	Se	S
			XVIII	Me	Se	S
			XIX	OMe	Se	S

	R	X		R	R ¹	X = X ¹		R	R ¹	X	X ¹
XX	H	S	XXVI	H	H	S	XXXVIII	H	H	S	Se
XXI	Me	S	XXVII	Me	Me	S	XXXIX	Me	Me	S	Se
XXII	OMe	S	XXVIII	OMe	OMe	S	XL	OMe	OMe	S	Se
XXIII	H	Se	XXIX	H	Me	S	XLI	H	Me	S	Se
XXIV	Me	Se	XXX	H	OMe	S	XLII	H	OMe	S	Se
XXV	OMe	Se	XXXI	Me	OMe	S	XLIII	Me	OMe	S	Se
			XXXII	H	H	Se	XLIV	Me	H	S	Se
			XXXIII	Me	Me	Se	XLV	OMe	H	S	Se
			XXXIV	OMe	OMe	Se	XLVI	OMe	Me	S	Se
			XXXV	H	Me	Se					
			XXXVI	H	OMe	Se					
			XXXVII	Me	OMe	Se					

Scheme 1 (Continued)

	R	X
XLVIII	H	S
XLIX	Me	S
L	OMe	S
LI	H	Se
LII	Me	Se
LIII	OMe	Se

Quaternary salts (II—VII)

The product obtained by heating for two hours at 150°C of the heterocyclic base (2-methylbenzthiazole, -benzselenazole or the corresponding 5-substituted derivatives) with ethyl *p*-toluenesulfonate (in equimolar amount) was precipitated by pouring into acetone. The precipitate was triturated under acetone, decanted and recrystallized from ethanol.

N-Ethyl-2-(tetrahydrofurylacetonilidene)-5-*R*-benzthiazoles and -benzselenazoles (VIII—XIII)

To a solution of the quaternary salt (II—VII), (0.1 mole) in pyridine (50 ml) tetrahydrofurylacetyl chloride (I), (0.1 mole) was added with stirring while the temperature was kept at 0°C. The stirring and cooling was continued for 30 minutes and pyridine was removed under diminished pressure. The residue was poured into water and the separated oil was extracted with benzene. Concentration of the benzene solution and purification of the crude product by chromatography on alumina gave, after crystallization from ethanol, the pure material.

N-Ethyl-2-(tetrahydrofurylthioacetonilidene-5-*R*-benzthiazole and -benzselenazole derivatives (XIV—XIX)

To a boiling solution of the acetonilidene compound (XIII—XVIII), (1 mole) in pyridine (500 ml) phosphorus pentasulfide (0.5 mole) was added portionwise. The mixture was refluxed for thirty minutes and pyridine was distilled off. The residue was poured into water (1500 ml) and the oil, which usually crystallized on standing, was separated, repeatedly extracted with benzene (3 × 500 ml) which was subsequently removed and the solid residue crystallized from ethanol.

2-(β-Methylmercapto-β-tetrahydrofurfuryl)vinylbenzthiazole and -benzselenazole ethiodides (XX—XXV)

Methyl iodide (0.115 mole) was added at room temperature to a solution of the thioacetonilidene compound (XIV—XIX), (0.1 mole) in dry benzene (300—500 ml). The mixture was stirred and the crystalline precipitate of the quaternary salt was collected after several hours by filtration, sucked dry, washed with acetone and crystallized from ethanol.

Meso-tetrahydrofurfurylthia- and -selenacarbocyanines (XXVI—XLVI)

An equimolar amount of 2-(β-methylmercapto-β-tetrahydrofurfuryl)vinylbenzthiazole or -benzselenazole ethiodide (XX—XXV) and 2-methylbenzthiazole or -benzselenazole

Table 1

Basic characteristics of the synthesized compounds (II–LIII)

No.	Formula	<i>M</i>	% N		Yield [%]	M.p. [°C]
			calculated	found		
II	C ₁₇ H ₁₉ NO ₃ S ₂	349.45			85	160–162
III	C ₁₈ H ₂₁ NO ₃ S ₂	363.47			87	183–184
IV	C ₁₈ H ₂₁ NO ₄ S ₂	379.47			79	163–165
V	C ₁₇ H ₁₉ NO ₃ SSc	396.26			78	123–125
VI	C ₁₈ H ₂₁ NO ₃ SSc	410.29			82	179–181
VII	C ₁₈ H ₂₁ NO ₄ SSc	426.29			81	168–170
VIII	C ₁₆ H ₁₉ NO ₂ S	289.38	4.86	4.69	86.5	oil
IX	C ₁₇ H ₂₁ NO ₂ S	303.40	4.63	4.64	84.3	107–108
X	C ₁₇ H ₂₁ NO ₃ S	319.41	4.40	4.57	57.5	84–86
XI	C ₁₆ H ₁₉ NO ₂ Se	337.28	4.18	4.26	58.9	oil
XII	C ₁₇ H ₂₁ NO ₂ Se	351.30	4.01	3.81	44.2	121–122
XIII	C ₁₇ H ₂₁ NO ₃ Se	367.30	3.84	4.08	31.9	oil
XIV	C ₁₆ H ₁₉ NOS ₂	305.44	4.60	4.45	31.5	oil
XV	C ₁₇ H ₂₁ NO ₂ S ₂	319.46	4.40	4.39	76.2	151–153
XVI	C ₁₇ H ₂₁ NO ₂ S ₂	335.47	4.19	4.12	72.0	165–167
XVII	C ₁₆ H ₁₉ NOSSe	352.34	4.99	3.81	60.9	oil
XVIII	C ₁₇ H ₂₁ NOSSe	366.36	3.83	3.77	82.2	148–149
XIX	C ₁₇ H ₂₁ NO ₂ SSc	382.36	3.67	3.62	54.2	117–119
XX	C ₁₇ H ₂₂ INOS ₂	447.39	3.14	3.10	68.2	159–162
XXI	C ₁₈ H ₂₄ INOS ₂	461.41	3.04	2.99	94.2	188–190
XXII	C ₁₈ H ₂₄ INO ₂ S ₂	477.41	2.95	2.83	58.5	176–178
XXIII	C ₁₇ H ₂₂ INOSSe	494.29	2.84	2.78	46.7	195–196
XXIV	C ₁₈ H ₂₄ INOSSe	508.31	2.76	2.68	50.4	207–209
XXV	C ₁₈ H ₂₄ INO ₂ SSc	524.31	2.68	2.62	41.9	188–190
XXVI	C ₂₆ H ₂₉ IN ₂ OS ₂	576.54	4.86	4.79	90.8	168–170
XXVII	C ₂₈ H ₃₃ IN ₂ OS ₂	604.59	4.64	4.55	92.4	203–205
XXVIII	C ₂₈ H ₃₃ IN ₂ O ₃ S ₂	636.59	4.40	4.37	65.6	222–224
XXIX	C ₂₇ H ₃₁ IN ₂ OS ₂	590.60	4.76	4.63	91.5	201–203
XXX	C ₂₇ H ₃₁ IN ₂ O ₂ S ₂	606.59	4.62	4.65	95.0	142–144
XXXI	C ₂₈ H ₃₃ IN ₂ O ₂ S ₂	620.59	4.52	4.71	88.4	203–205
XXXII	C ₂₆ H ₂₉ IN ₂ OSe ₂	670.34	4.18	4.05	51.6	163–165
XXXIII	C ₂₈ H ₃₃ IN ₂ OSe ₂	698.39	4.02	3.83	59.4	153–155
XXXIV	C ₂₈ H ₃₃ IN ₂ O ₃ Se ₂	730.39	3.84	3.87	45.9	213–214
XXXV	C ₂₇ H ₃₁ IN ₂ OSe ₂	684.36	4.10	3.96	50.4	178–179
XXXVI	C ₂₇ H ₃₁ IN ₂ O ₂ Se ₂	700.36	4.00	4.07	52.7	134–136
XXXVII	C ₂₈ H ₃₃ IN ₂ O ₂ Se ₂	714.38	3.92	3.90	58.0	153–155
XXXVIII	C ₂₆ H ₂₉ IN ₂ OSSc	623.44	4.50	4.35	61.9	144–146
XXXIX	C ₂₈ H ₃₃ IN ₂ OSSc	651.49	4.30	4.27	73.8	207–209
XL	C ₂₈ H ₃₃ IN ₂ O ₃ SSc	683.49	4.10	4.15	88.5	247–248
XLI	C ₂₇ H ₃₁ IN ₂ OSSc	637.46	4.40	4.36	73.4	130–131
XLII	C ₂₇ H ₃₁ IN ₂ O ₂ SSc	653.46	4.30	4.42	71.6	180–182
XLIII	C ₂₈ H ₃₃ IN ₂ O ₂ SSc	667.48	4.21	3.98	78.5	196–198
XLIV	C ₂₇ H ₃₁ IN ₂ OSSc	637.46	4.40	4.48	81.9	208–209
XLV	C ₂₇ H ₃₁ IN ₂ O ₂ SSc	653.46	4.30	4.41	75.7	260–262
XLVI	C ₂₈ H ₃₃ IN ₂ O ₂ SSc	667.48	4.21	4.09	60.4	206–208
XLVIII	C ₂₁ H ₂₄ N ₂ O ₂ S ₃	432.59	6.50	6.38	53.1	176–178
XLIX	C ₂₂ H ₂₆ N ₂ O ₂ S ₃	446.62	6.30	6.17	77.1	188–189
L	C ₂₂ H ₂₆ N ₂ O ₃ S ₃	462.62	6.08	6.11	88.2	170–172
LI	C ₂₁ H ₂₄ N ₂ O ₂ S ₂ Se	479.49	5.86	5.78	27.3	153–155
LII	C ₂₂ H ₂₆ N ₂ O ₂ S ₂ Se	493.51	5.70	5.63	30.2	230–231
LIII	C ₂₂ H ₂₆ N ₂ O ₃ S ₂ Se	509.51	5.52	5.45	98.3	236–238

Table 2

Absorption (spectral) maxima of the compounds (XXXII—XLVI)

No.	Abs. max. [nm]	Shift to <i>meso</i> -H	Deviation
XXXII	568	—	—
XXXIII	572	+ 4	—
XXXIV	585	+17	—
XXXV	570	+ 2	—
XXXVI	576	+ 8	—0.5
XXXVII	579	+11	+0.5
XXXVIII	560	—	—1.5
XXXIX	568	+ 8	—0.5
XL	579	+19	—1.0
XLI	564	+ 4	—
XLII	569	+ 9	—1.0
XLIII	574	+14	—
XLIV	565	+ 5	—1.5
XLV	571	+11	—0.5
XLVI	576	+13	—0.5

ethiodide was dissolved in hot methanol, cooled to room temperature and an equimolar amount of triethylamine was added. The mixture was stirred overnight and the separated dye was filtered, washed with ether—ethanol (3 : 1), and recrystallized from ethanol.

α-Tetrahydrofurfuryldimethinemerocyanines (XLVIII—LIII)

A mixture of equimolar amounts of 2-(β-methylmercapto-β-tetrahydrofurfuryl)vinyl-benzthiazole or -benzselenazole ethiodide (XX—XXV) and 3-ethylrhodanine (XLVII) dissolved in a minimum of ethanol—piperidine was heated under reflux. The separated dye was collected by filtration, washed with ether—methanol (3 : 1), air-dried, and purified by chromatography, or directly crystallized from methanol.

Results and discussion

A characteristic band with a pronounced maximum is present in the absorption curve of the polymethine dyes. In spectral evaluation of the cyanine dyes important factors to be considered are the basicity of the heteroaromatic rings [5, 6], electronic contributions of the substituents present in the aromatic parts of the molecule as well as the substituents in the *meso*-position of the polymethine chain [7—10].

Taking into consideration the function pK_a vs. $\bar{\nu}(C=O)$ or σ^* electronegativity of the value 2.3 and Taft's substitution constant $\sigma^* = 0.4$ was assigned [11] to the tetrahydrofurfuryl group; both parameters are close to the corresponding values of hydrogen as a substituent. Thus, it can be expected that in such complex systems as the compounds (XXVI—XLVI) the electron effects of the $C_4H_7OCH_2$ group should not be well pronounced. Accordingly, on the spectrum of the basic dye with the *meso*-tetrahydrofurfurylthiacarbocyanine structure (XXVI) a band with λ_{max} 555 nm can be seen and a structure, analogous to the latter, non-substituted in the *meso*-position [2, 12] shows this maximum at 557 nm. The locations of the absorption maxima on the spectra of other dyes belonging to this group, affected by the substituents R and R¹ in the position 5 or 5' are those

expected: compared to the substances having an atom of hydrogen in the *meso*-position the shifts of the absorption maxima are +8, +20, +3, +9, and +12 nm for compounds *XXVII*, *XXVIII*, *XXIX*, *XXX*, and *XXXI*, respectively. When the dye contains only one substituent in the position 5 (Me in *XXIX*, MeO in *XXX*) the bathochromic shift is half of the former and the deviation is almost negligible. The value of the deviation observed in the case of other dyes is still within the range of the experimental errors. It can be seen from Table 2 that the symmetrical and the non-symmetrical selenacarbo-cyanines (*XXXII*–*XLVI*) show the same type of effects of the substitution in the position 5 as showed by the thiacarbo-cyanines. A small difference between the calculated values, and those found, of the absorption maxima of the *meso*-tetrahydrofurfurylthia-selenacarbo-cyanines (*XXXVIII*–*XLVI*) is in agreement with small differences in the basicity of these two heteroaromatic systems.

α -Substituted (H, Me, Et) dimethinemerocyanines show absorption maxima at 524, 532, and 536 nm. From the values of the absorption maxima for compounds *XLVIII*–*LIII* (542, 543.5, 544, 540, 541, and 542 nm, respectively) it can be concluded that the tetrahydrofurfuryl group located in the α -position of a simpler molecule is responsible for the differences in the electron density and thus the shifts of the absorption maxima. The reflexion spectrum of 3,3'-diethyl-9-methylthiacarbo-cyanine, one of the most powerful optical sensitizer of photographic emulsions based on silver halides, is shown

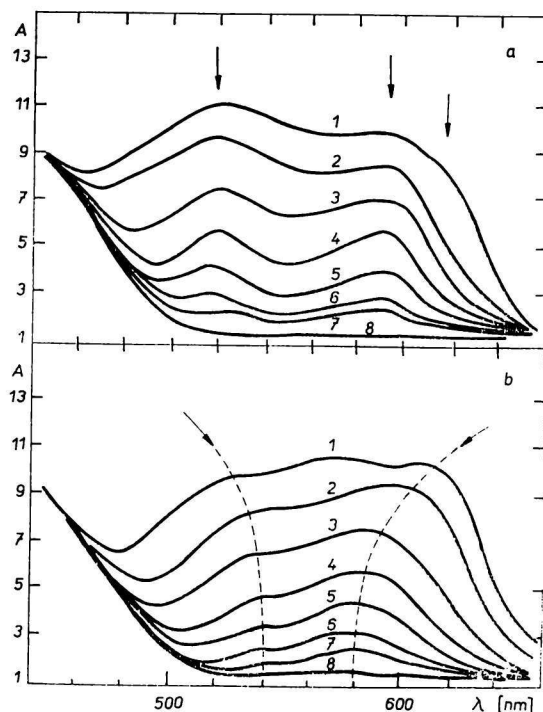


Fig. 1. Reflexion spectra of 3,3'-diethyl-9-methylthiacarbo-cyanine iodide (a) and 3,3'-diethyl-9-tetrahydrofurfurylthiacarbo-cyanine iodide (b) on the surface of a micro-crystal of AgHal at the concentrations of emulsions (mg/kg).

1. 160; 2. 80; 3. 40; 4. 20; 5. 10; 6. 5; 7. 2.5; 8. reference unsensitized emulsion.

in Fig. 1a. It can be clearly seen here that this dye exists in a number of states of polyaggregation, mainly H , absorbing at 520 nm, and J_1 absorbing at 595 nm. At the maximum concentration (curve 1) the J_2 maximum is still visible at 620 nm. From the course of curves of the reflexion spectrum of XXVI, taken at the same concentration (Fig. 1b) it is obvious that here the formation of clear-cut types of states of polyaggregation does not occur. The practical comparison of these two dyes as to the sensitizing efficacies substantiates the previous findings [13] according to which the H states are ineffective in photography. The most effective are the individual J states and therefore the compound XXVI, though it widens the sensitivity range of silver halides, does not increase the absolute value of sensitivity thereof. Thus, this dye can be considered a very weak optical sensitizer. Based on practical tests [14], this conclusion holds also in the case of other polymethine dyes bearing a tetrahydrofurfuryl group as a substituent of the polymethine chain.

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