SYNTHESIS AND PROPERTIES OF INDOLO-3,3'-TRIMETHINECYANINES SUBSTITUTED IN THE POLYMETHINE CHAIN AND HETERORINGS

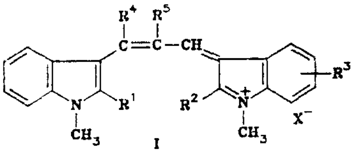
T. M. Karymova, P. I. Abramenko,
and L. G. Kurkina

UDC 547.753'754'757.07:543.422.6:541.651

New 8-chloro-, 9-cyano-, and 8-methyl-9-carboxy-substituted (in the outer polymethine chain), indolo-3,3'-trimethinecyanines containing substituents in the 2, 5, or 7 position of the indole heteroresidues were synthesized, and their spectral, polarographic, and photographic properties were studied. It is shown that electron-acceptor substituents in the 2 and 2' positions of the indole heteroresidues and the 8 and/or 9 positions of the polymethine chain of the dye molecules that do not have steric hindrance give rise to a bathochromic shift of their absorption maxima. 8-Chloro-, 9-cyano- and 8-methyl-9-carbethoxyindolo-3,3'-trimethinecyanines with electron-acceptor groups in the 2 and 2' positions are ineffective sensitizers of direct positive silver halide emulsions.

The effect of halogen atoms and alkyl groups in the meso position and of alkyl and aryl groups in the 8(10) positions of the outer polymethine chain of indolo-3,3'-trimethinecyanines — spectral sensitizers of direct positive silver halide materials — on their spectral, polarographic, and photographic properties has been previously studied [1, 2].

In the present paper we describe the synthesis and spectral, polarographic, and photographic properties of new indolo-3,3'-trimethinecyanines substituted in the polymethine chain and heteroresidues (I):



I

I $R^1=H, C_6H_5$; $R^2=H, C_6H_5, COOH, COOC_2H_5, COOCH_3$, p-$BrC_6H_4$, p-$CH_3C_6H_4$; $R^3=H, Cl, NO_2, CH_3$; $R^4=H, CH_3, Cl$; $R^5=H, Cl, COOC_2H_5$; $X=CiO_4, Br, C_7H_7SO_3$

Symmetrical indolotrimethinecyanines that do not have substituents in the outer polymethine chain (Iw, x,* $R^4 = R^5 = H$) were obtained by the reaction of 1-methylindoles with tetraethoxypropane in acetic anhydride in the presence of p-toluenesulfonic acid (p-TSA) with subsequent conversion of the tosylate to the perchlorate.

The new indolo-3,3'-trimethinecyanines substituted in the polymethine chain and heteroresidues were synthesized via the general scheme. (See scheme on following page.)

The symmetrical and unsymmetrical indolotrimethinecyanines with a nitrile group in the meso position (I, $R^4 = H$, $R^5 = CN$) were synthesized by the reaction of 1-methyl-2-R^1-indoles with 2-cyano-3-dimethylaminoacrolein in anhydrous benzene with the addition of acetyl chloride and subsequent condensation of 1-methyl-2-R^1-3-(2'-cyano-2'-formylvinyl)indoles II with 1-methyl-2-R^2-7-R^3-indoles in acetic anhydride or nitromethane in the presence of p-TSA with subsequent conversion of the tosylate to the perchlorate.

The 8-chloroindolotrimethinecyanines (I, $R^4 = Cl$) were obtained via the following scheme. The reaction of 1-methyl-2-R^1-3-acetylindoles with phosphorus pentachloride and dimethylforma-

---

*See Table 1 for the expansion of the designations Ia-x.

Kazan Scientific-Research Technological and Planning Institute of the Photographic-Chemical Industry, Kazan 420035. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 897-901, July, 1988. Original article submitted January 28, 1987; revision submitted July 27, 1987.

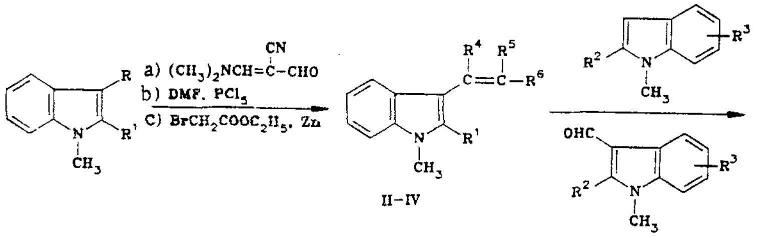
0009-3122/88/2407-0736$12.50

TABLE 1. Spectral and Polarographic Characteristics of Indo-3,3'-trimethinecyanines I

Compound*	R^1	R^2	R^3	R^4	R^5	λ_{max}*, nm†	$\varepsilon \cdot 10^{-4}$	$E_{1/2}Ox$, V	$-E_{1/2}Red$, V
	H	H	H	H	H	570	8,5	—	—
	C_6H_5	C_6H_5	H	H	H	592 [2]	10	1,14	0,26
	C_6H_5	C_6H_5	H	H	Cl	610 [2]	4,7	1,12	0,21
	C_6H_5	C_6H_5	H	H	CH_3	612 [2]	7,8	—	—
	C_6H_5	C_6H_5	H	CH_3	H	605 [2]	6,5	1,21	0,48
	C_6H_5	C_6H_5	H	C_6H_5	H	625 [2]	19	1,20	0,45
	CH_3	CH_3	H	H	H	568 [2]	13,25	1,17	0,41
Ia	H	H	H	H	CN	592	10,4	1,38	0,10
Ib	H	C_6H_5	H	H	CN	596	4,0	1,41	0,08
Ic	H	COOH	H	H	CN	590	13,4	1,39	0,08
Id	H	$COOC_2H_5$	7-Cl	H	CN	590	12,5	1,43	0,04
Ie	H	H	7-NO_2	H	CN	590	8,5	1,42	+0,03
If	C_6H_5	C_6H_5	H	H	CN	586 [2]	10,0	1,04	—
Ig	C_6H_5	p-BrC_6H_4	H	H	CN	588	8,2	1,44	0,10
Ih	C_6H_5	COOH	H	H	CN	584	8,0	1,40	0,12
Ii	C_6H_5	$COOC_2H_5$	7-Cl	H	CN	584	8,9	1,46	0,07
Ij	C_6H_5	H	7-NO_2	H	CN	582	8,9	1,50	0,10
Ik	H	H	H	Cl	H	602	8,75	1,25	0,11
Il	H	C_6H_5	H	Cl	H	612	8,63	1,30	0,08
Im	H	CH_3	5-CH_3	Cl	H	596	8,75	1,48	0,04
In	H	$COCH_3$	H	Cl	H	622	2,75	1,44	0,05
Io	C_6H_5	C_6H_5	H	Cl	H	636	1,90	1,36	0,15
Ip	C_6H_5	CH_3	5-CH_3	Cl	H	620	2,40	1,28	0,20
Iq	C_6H_5	$COOCH_3$	H	Cl	H	638	2,10	1,42	0,12
Ir	C_6H_5	C_6H_5	H	CH_3	$COOC_2H_5$	618	12,5	1,28	0,30
Is	C_6H_5	C_6H_5	5-NO_2	CH_3	$COOC_2H_5$	614	2,7	—	—
It	C_6H_5	CH_3	5-CH_3	CH_3	$COOC_2H_5$	600	6,4	—	—
Iu	C_6H_5	H	7-NO_2	CH_3	$COOC_2H_5$	576	1,3	—	—
Iv	C_6H_5	p-$CH_3C_6H_4$	H	CH_3	$COOC_2H_5$	616	8,6	—	—
Iw	$COOC_2H_5$	$COOC_2H_5$	H	H	H	632	4,9	—	—
Ix	COOH	COOH	H	H	H	628	2,6	—	—

*Ia-j, m-x X = ClO_4; Ik X = Ts; Iℓ X = Br.

†The λ_{max} values were measured in nitromethane–acetic acid (5:1).



Ia $R^4=H$; $R^5=CN$; $R=H$; $R^1=H$, C_6H_5; $R^2=H$; C_6H_5, p-BrC_6H_4, COOH, $COOC_2H_5$; $R^3=$7-Cl, 7-NO_2; $R^6=CHO$; $X=ClO_4$; Ib $R^4=Cl$; $R^5=H$; $R=COCH_3$; $R^1=H$, C_6H_5; $R^2=H$, CH_3, C_6H_5, $COOCH_3$; $R^3=$5-CH_3; $R^6=CHO$; $X=ClO_4$, Ts, Br; Ic $R^4=CH_3$; $R^5=$ $=COOC_2H_5$; $R=COCH_3$; $R^1=C_6H_5$; $R^2=H$, CH_3, C_6H_5, p-$CH_3C_6H_4$; $R^3=H$, 7-NO_2, 5-CH_3; $R^6=H$; $X=ClO_4$

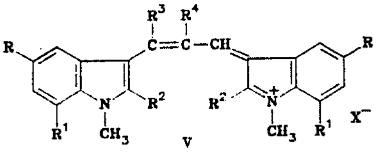
mide by the Vilsmeier method was used to synthesize 3-(1'-methyl-2'-R^1-3-indolyl)-3-chloro-2-propen-1-als III [3], the condensation of which with 1-methyl-2-R^2-5-R^3-indoles in nitromethane (or acetic anhydride) with the addition of a mineral (or organic) acid gave indolotrimethinecyanines with a chlorine atom in the 8 position.

For the synthesis of both symmetrical and unsymmetrical 8-methyl-9-carbethoxyindolotrimethinecyanines ethyl 3-(1'-methyl-2'-R^1-3-indolyl)crotonates IV were condensed with 1-methyl-2-R^2-5(or 7)-R^3-3-formylindoles at room temperature in acetic anhydride in the presence of perchloric acid.

The dyes are formed in good yields. In some cases side products in the synthesis of the trimethinecyanines are indolomonomethinecyanines, which are removed by treatment of the reaction product with benzene–methanol (20:1). The starting ethyl 3-(1'-methyl-2'-R^1-3-indolyl)crotonates IV were obtained by the reaction of 1-methyl-2-R^1-3-acetylindoles with ethyl monobromoacetate in the presence of activated zinc [4].

Peaks of ions corresponding to $[M - HX]^+$ ions and peaks that indicate the presence of an alkyl group attached to the nitrogen atom of the indole heteroresidue and the substituted

TABLE 2. Charges on the Atoms of the Chromophore in the Molecules of the Dyes with Structure V:



V

R	R^1	R^2	R^3	R^4	$q_r(^1S_0$ state)				
					$N_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(8)}$	$C_{(9)}$
H	H	H	H	H	0,311	0,111	−0,085	0,216	−0,045
H	H	C_6H_5	H	H	0,288	0,101	−0,083	0,180	−0,048
H	H	C_6H_5	H	Cl	0,307	0,089	−0,078	0,200	−0,038
H	H	COOH	H	H	0,321	0,091	−0,070	0,180	−0,036
H	H	H	Cl	H	0,304	0,099	−0,088	0,185	−0,039
H	H	H	H	CN	0,320	0,101	−0,084	0,201	−0,048
CH_3	H	H	H	H	0,308	0,109	−0,086	0,214	−0,046
H	NO_2	H	H	H	0,315	0,113	−0,087	0,218	−0,042

indole ring in the structure of the dye molecule are characteristic for the mass spectra of the indolotrimethinecyanines.

The data in Table 1 show that carboxy and carbethoxy groups in the 2 and 2' positions of the indolo-3,3'-trimethinecyanines (Iw, x) give rise to a significantly greater bathochromic effect (58-62 nm) than a phenyl group (22 nm) [2]. The introduction of an electron-acceptor nitrile group in the meso position of the polymethine chromophore of unsubstituted (in the 2 and 2' positions of the indole heteroresidues) indolo-3,3'-trimethinecyanine (Ia) gives rise to a significant bathochromic shift of the absorption maximum (by 22 nm). However, the introduction of this group into 2,2'-disubstituted indolo-3,3'-trimethinecyanine (If), on the other hand, leads to a hypsochromic effect – evidently because of the steric hindrance of the substituents, which is absent in the case of the 2-monosubstituted dyes, as demonstrated by Stuart–Briegleb models of their molecules. The presence of a chlorine atom in the 8 position of the outer polymethine chain also gives rise to a bathochromic effect. Thus the bathochromic shift of the absorption maximum of 1,1'-dimethyl-2,2'-diphenyl-8-chloroindolo-3,3'-trimethinecyanine perchlorate (Io) is 44 nm. Dyes that contain methyl and carboxy groups in the 8 and 9 positions (Ir-v), respectively, are more weakly colored than the 8-chloro derivatives.

The results of quantum-chemical calculations [by the Pariser–Parr–Pople (PPP) method as described in [5], Table 2] show that distribution of the electron density in the chromophore with localization of the positive charge on the $N_{(1)}$, $C_{(2)}$, and $C_{(8)}$ atoms and of the negative charge on the $C_{(3)}$ and $C_{(9)}$ atoms is characteristic for the atoms of the chromophore of the indolo-3,3'-trimethinecyanines. A chlorine atom in the 9 position promotes more uniform distribution of the electron density in the chromophor; this corresponds to the experimentally observed bathochromic shift of the absorption maximum. It manifests chiefly an electronic effect [2], since steric hindrance is virtually insignificant here. The same is also characteristic for the 8-chloro derivatives. The nitrile group in the 9-cyano-substituted dyes gives rise to a decrease in the electron density and increases the uniformity of its distribution in the chromophore, which should lead to deepening of the color. However, as noted above, a hypsochromic effect occurs in the series of 9-cyano-2,2'-disubstituted cyanines, evidently because of steric hindrance. Electron-acceptor substituents in the 2 and 2' positions promote an increase in delocalization of the electron density in the chromophore, thereby giving rise to a bathochromic effect. Methyl groups in the 5 and 5' positions of the indole heteroresidues have little effect on the character of the charge distribution; this is also characteristic for a nitro group in their 7 and 7' positions. These substituents are evidently weakly conjugated with the π-electron system of the chromophore.

It follows from the data in Table 1 that smaller values of the polarographic reduction potentials and larger values of the polarographic oxidation potentials than in the series of 9-Y- and 8-Y'-substituted derivatives (Y = Cl, CH_3, $COOC_2H_5$; Y' = CH_3, C_6H_5) are characteristic for the dyes that contain a nitrile group in the 9 position and a chlorine atom in the 8 position in the polymethine chain. Low E^{Red} and E^{Ox} values are characteristic for the 9-cyanoindolo-3,3'-trimethinecyanines, particularly when electron-acceptor substituents are pres-

TABLE 3. Characteristics of the Dyes with Structure I

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
Ia	300*	62,1	4,1	9,7	$C_{22}H_{18}ClN_3O_4$	62,3	4,3	9,9	37
Ib	>300†	67,2	4,2	8,1	$C_{28}H_{22}ClN_3O_4$	67,4	4,4	8,4	49
Ic	>300*	58,8	3,7	8,8	$C_{23}H_{18}ClN_3O_6$	59,0	3,9	9,0	51
Id	>300†	56,5	3,8	—	$C_{25}H_{21}ClN_3O_6$	56,6	4,0	—	39
Ie	>300†	56,2	3,5	11,8	$C_{22}H_{17}ClN_4O_6$	56,4	3,6	11,9	25
Ig	209—210†	62,5	3,6	6,3	$C_{34}H_{25}BrClN_3O_6$	62,3	3,8	6,4	75
Ih	236—238†	63,7	4,2	6,9	$C_{29}H_{22}ClN_3O_6$	64,0	4,0	7,1	68
Ii	232—233‡	61,6	4,4	6,6	$C_{31}H_{25}Cl_2N_3O_6$	61,4	4,1	6,9	71
Ij	243—244**	61,7	3,6	10,0	$C_{28}H_{21}CiN_4O_6$	61,4	3,8	10,2	55
Ik	91—93**	66,5	5,0	5,5	$C_{28}H_{25}ClN_2O_2S$	66,6	5,0	5,5	95
Il	130—132†	66,0	4,3	5,4	$C_{27}H_{22}BrClN_2$	66,2	4,5	5,7	62
Im	175—178*	59,6	4,67	5,94	$C_{23}H_{22}Cl_2N_2O_4$	59,8	4,81	6,07	78
In	162—164†	—	—	5,5	$C_{23}H_{20}Cl_2N_2O_6$	56,2	4,1	5,7	59
Io	180—182†	67,6	4,2	4,6	$C_{33}H_{26}Cl_2N_2O_4$	67,7	4,5	4,8	63
Ip	175† (dec)	64,7	4,7	5,0	$C_{29}H_{26}Cl_2N_2O_4$	64,7	4,9	5,2	78
Iq	280—282†	61,2	4,1	4,7	$C_{29}H_{24}Cl_2N_2O_6$	61,4	4,2	4,9	62
Ir	151—153**	69,6	5,0	4,1	$C_{37}H_{35}ClN_2O_6$	69,7	5.2	4.4	81
Is	198—201†	64,9	4,5	6,3	$C_{37}H_{32}N_3ClO_8$	65,1	4,7	6,2	37
It	160—161†	67,0	5,4	4,5	$C_{33}H_{33}N_2ClO_6$	67,3	5,65	4,7	81
Iu	95—97†	61,2	4,4	6,7	$C_{31}H_{28}ClN_3O_8$	61,4	4,6	6,9	70
Iv	192—194†	69,9	5,2	4,1	$C_{38}H_{35}ClN_2O_6$	70,1	5,4	4,3	91
Iw	231—233**	58,3	4,40	5,40	$C_{25}H_{23}ClN_2O_8$	58,31	4,51	5,41	62
Ix	203—205**	56,62	3,53	5,61	$C_{23}H_{18}CiN_2O_8$	56,81	3,70	5,76	24

*Violet prisms.

†Dark-blue prisms.

‡Dark-violet prisms.

**Dark-green prisms.

ent in the 2(2') and/or 7(7') positions of the indole rings. The results of an investigation of the photographic properties of the dyes obtained show that 8-chloro(methyl)-9-cyano(carbethoxy)indolo-3,3'-trimethinecyanines with electron-acceptor groups in the above-indicated positions of the indole heteroresidues are ineffective sensitizers of direct positive silver halide photoemulsions; this corresponds to their extremely low E^{Red} and high E^{Ox} values. With respect to effectiveness they are significantly inferior to dyes that contain an alkyl (aryl) group or a chlorine atom as a substituent, respectively, in the 8 or 9 position of the polymethine chain and a phenyl or substituted phenyl group in the 2 and 2' positions of the indole rings.

EXPERIMENTAL

The spectra of the dyes were measured with an SF-10 spectrophotometer. The mass spectra were recorded with a Varian MAT-311A spectrometer at an ionizing voltage of 70 meV, a cathode-emission current of 300 μA, and an accelerating voltage of 3 kV. The polarographic characteristics were determined by the method described in [1].

Indolotrimethinecyanines (I, $R^4 = R^5 = H$). A 0.01-mole sample of p-TSA was added in portions to a solution of 0.02 mole of 1-methyl-2-R-indole and 0.01 mole of 1,1,3,3-tetraethoxypropane in acetic anhydride, and the mixture was stirred for 3 h at room temperature. A 0.2-ml sample of perchloric acid was then added, after which the mixture was allowed to stand for 15 min. It was then diluted with ether, and the precipitate was removed by filtration, washed with ether, and dried. The dye was purified by recrystallization from ethanol and dried in vacuo at 80°C (Table 3).

meso-Cyanoindolo-3,3'-trimethinecyanines. A mixture of 0.001 mole of 1-methyl-2-R^1-3-(2'-cyano-2'-formylvinyl)indole (II), 0.001 mole of 1-methyl-7-R^3-indole, 20 ml of acetic anhydride, and 0.001 mole of p-TSA was stirred for 3 h at room temperature, after which 0.5 ml of perchloric acid was added. After 20 min, the mixture was diluted with ether, and the precipitate was removed by filtration and washed with ether. The dyes were purified by reprecipitation from nitromethane (Table 3).

8-Chloroindolo-3,3'-trimethinecyanines. A 0.1-ml sample of 70% perchloric (hydrobromic) acid or p-TSA was added dropwise at room temperature to a mixture of 0.0003 mole of 3-(1'-methyl-2'-R^1-3-indolyl)-3-chloro-2-propen-1-al III, 0.0003 mole of 1-methyl-2-R^2-5-R^3-indole, and 10 ml of acetic anhydride (or benzene), and the mixture was maintained at room temperature for 2-3 h. It was then poured into 100 ml of ether, and the precipitate was removed by filtration and washed with ether. The dyes were purified by reprecipitation from acetic anhydride (Table 3).

8-Methyl-9-carbethoxyindolo-3,3'-trimethinecyanines. A mixture of 0.0004 mole of ethyl 3-(1'-methyl-2'-R^1-3-indolyl)crotonate IV, 0.0004 mole of 1-methyl-2-R^2-5(7)-R^3-3-formylindole, and 15 ml of acetic anhydride was stirred at room temperature until the solids had dissolved completely, after which 0.1 ml of 70% perchloric acid was added dropwise. After 2-3 h, the mixture was diluted with ether. The precipitate was removed by filtration and washed with ether. The dyes were purified by reprecipitation from nitroethane (Table 3).

LITERATURE CITED

1. T. N. Galiullina, P. I. Abramenko, A. V. Kazymov, and V. M. Gorokhovskii, Khim. Geterotsikl. Soedin., No. 8, 1067 (1981).
2. T. N. Galiullina and P. I. Abramenko, Khim. Geterotsikl. Soedin., No. 12, 1652 (1983).
3. N. N. Suvorov, A. B. Kalinskii, and Yu. I. Smushkevich, Zh. Obshch. Khim., 13, 197 (1977).
4. M. Baron, P. Cointet, and G. Bauduin, Bull. Soc. Chim. France, Part II, Nos. 7-8, 369 (1977).
5. P. I. Abramenko, T. N. Galiullina, and A. N. Gusarov, Collection of Scientific Research of the Kazan Scientific-Research Technological and Planning Institute of the Photographic-Chemical Industry [in Russian], Moscow (1980), p. 126.

REACTION OF 2-METHYLENE-2,3-DIHYDROINDOLES WITH ACRYLAMIDE

A. A. Shachkus and Yu. A. Degutis

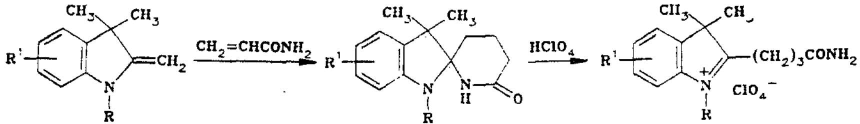
UDC 547.828'753:543.422

1,3-Dihydrospiro[2H-indolo-2,2'-piperidine] derivatives were obtained by the reaction of 2-methylene-2,3-dihydro-1H-indole derivatives with acrylamide in proton-containing solvents. 2-(3-Carbamoylpropyl)-3H-indolium perchlorates were formed when the 1,3-dihydrospiro[2H-indolo-2,2'-piperidine] derivatives were treated with perchloric acid.

Alkylation of enamines by induced addition is often used in the preparation of various heterocyclic compounds [1-3]. It is known that condensed heterocyclic systems containing a lactam ring are formed in the reaction of pyrrolidine-series endo-enamines with acrylamide [4, 5].

The purpose of the present paper is an investigation of the reaction of acrylamide with indoline enamines Ia-d.

1,3-Dihydrospiro[2H-indolo-2,2'-piperidine] derivative IIa is formed during heating of a mixture of 2-methylene-2,3-dihydro-1H-indole (Ia) with acrylamide in ethylene or diethylene glycol. We can assume that the first stage of this reaction is the addition of acrylamide to the β-carbon atom of the enamine group with the formation of a Michael adduct, which then undergoes ring closure to spiro compound IIa. The proton-containing solvent participates in the reaction during proton transfer. 1,3-Dihydrospiro[2H-indolo-2,2'-piperidines] IIb-d are obtained similarly to compound IIa.



Ia-d IIa-d IIIa-d

I—III a–b $R=CH_3$, d $R=C_2H_5$; a, d $R^1=H$, b $R^1=5\text{-}CH_3$, c $R^1=7\text{-}CH_3$

A. Snechkus Kaunas Polytechnic Institute, Kaunas 233006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 902-904, July, 1988. Original article submitted January 12, 1987.

0009-3122/88/2407-0740$12.50