SYNTHESIS AND PROPERTIES OF SUBSTITUTED INDOLO-3,3'-TRIMETHINECYANINES

T. N. Galiullina and P. I. Abramenko

UDC 668.819.45:547.752'753.07: 543.253'422.6'51

Some new indolo-3,3'-trimethinecyanines, derived from 1,2-dimethyl and 1-methyl-2arylindole and substituted in the external polymethine chain with halogen, methyl, aryl, and cyano, have been synthesized. The effects of the substituents in the external polymethine chain on the spectral characteristics of the indolotrimethinecyanines are discussed, taking into account delocalization of electron density in the chromophore and steric effects, together with the polarographic and photographic properties of these dyes.

We have previously considered the effects of halogen atoms in the mesopositions of the external polymethine chain in symmetrical indolo-3,3-trimethinecyanines (which are spectral sensitizers for direct positive silver halide photographic emulsions) on their spectral, polarographic, and photographic properties, and we have studied the electronic structures of these dyes [1-3].

We here describe the synthesis and spectral and polarographic properties of some new indolo-3,3'-trimethinecyanines substituted in the polymethine chain (I):



 $\begin{array}{c} R^1 = CH_3, \ C_6H_5, \ p \cdot CH_3C_6H_4, \ p \cdot CH_3OC_6H_4 \ or \\ R^3 = H, \ CH_3 \ or \\ CN; \ R^4 = H \ or \\ CH_3, \ X^- - anion \end{array}$

Reaction of (II) with 2-cyano-3-dimethylaminoacrolein in benzene containing acetyl chloride gave 1-methyl-2-phenyl-3-(2-cyano-2-formyvinyl)indole (III), which was condensed with a second molecule of (II) in nitromethane in the presence of TSA to give the dye with a cyano-group in the meso-position of the external polymethine chain (I, $R^3 = CN$).

Reaction of (II) with 2-phenylazomalondialdehyde in acetic acid in the presence of TSA afforded a mixture of the carbinol (IVa) [1,3-bis-(1-methyl-2-phenylindol-3-yl)-2-phenylazo-3-hydroxy-1-propene] with, apparently, 9-phenylazo-(I) ($R^1 = C_6H_5$, $R_3 = N_2C_6H_5$). Similarly, the sodium salt of nitromalondialdehyde gave a mixture of the carbinol (IVb) [1,3-bis-(1-methyl-2-phenylindol-3-yl)-2-nitro-3-hydroxy-1-propene] and, probably, 9-nitro-(I) ($R^1 = C_6H_5$, $R^3 = NO_2$).

All-Union State Scientific-Research and Planning Institute for the Chemical and Photographic Industries, Moscow 125167. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1652-1656, December, 1983. Original article submitted January 20, 1983.

Com- pound		λ _{max} ,	e _{max} ,	$E_{1} O x$,	$E_{1/2}Red$				
	R ¹	R²	R ³	R4	X	nm	×10 ⁴	В	В
Ia Ib Ic If If Ih Ii Ik Im In In Ip Ir Is	$\begin{array}{c} CH_{3}\\ CH_{3}\\ CH_{3}\\ CH_{3}\\ CH_{3}\\ C_{4}H_{5}\\ C_{6}H_{5}\\ P^{-}BrC_{6}H_{4}\\ C_{6}H_{5}\\ C_{6}H_{5}\\ P^{-}BrC_{6}H_{4}\\ P^{-}CH_{3}OC_{6}H_{4}\\ C_{6}H_{5}\\ \end{array}$	$\begin{array}{c} H \\ H $	H CH ₃ Cl Br H H CH ₃ CH ₃ Cl Br Br Br H H H H H H H H CN	HHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHH	$\begin{array}{c} CI\\ CI\\ CI\\ CI\\ CI\\ CI\\ CI\\ CI\\ CI\\ CI\\$	$\begin{array}{c} 568 \ [2] \\ 580 \\ 592 \ [2] \\ 568 \ [2] \\ 615 \\ 592 \ [2] \\ 605 \\ 610 \ [2] \\ 598 \ [2] \\ 598 \ [2] \\ 598 \ [2] \\ 598 \ [2] \\ 605 \\ 630 \\ 625 \\ 628 \\ 628 \\ 628 \\ 628 \\ 586 \end{array}$	$\begin{array}{c} 13,25\\7,5\\11,5\\14,5\\4,87\\10,0\\7,8\\6,7\\4,7\\15,0\\10,68\\9,62\\6,5\\4,5\\19,0\\10,0\\10,0\\10,2\\10,0\end{array}$	1,17 0,66 0,38 1,15 1,14 1,12 1,18 1,05 1,10 1,21 1,20 1,10 1,15	$\begin{array}{c} 0,41\\ 0,93\\ 0,48\\ 0,42\\ 0,26\\ 0,21\\ 0,24\\ 0,25\\ 0,40\\ 0,48\\ 0,45\\ 0,35\\ 0,50\\ \end{array}$

TABLE 1. Spectral and Polarographic Properties of Indolotrimethinecyanines (I)

<u>Note.</u> Measurements of $E_1/2^{\infty}$ and $E_1/2^{\text{Red}}$ were made at glass-graphite and mercury electrodes respectively, by the method described in [2]. λ_{max} values were measured in a 5:1 mixture of nitromethane and acetic acid.



 $IV a R^3 = N_2C_6H_5$, b R³ = NO₂

However, only the carbinols were isolated from the reaction mixture, since the corresponding dyes (I), apparently as a result of the reduced acidity of the medium (during isolation), were reconverted into (IVa, b). The spectral characteristics of the dyes in a 5:1 mixture of nitromethane and acetic acid are given in Table 1, from which it will be seen that in the case of 2,2'-dimethylindolo-3,3'-trimethinecyanines, the introduction of a methyl group into the meso-position of the external polymethine chain, like chlorine, results in a bathochromic shift of the absorption maximum. In this connection chlorine causes a greater bathochromic shift, whereas 9-bromoindolo-3,3'-trimethinecyanines has the same color as the unsubstituted dye. In the 2,2'-diphenylindolo-3,3'-trimethinecyanines, however, the value of the bathochromic shift following the introduction of a chlorine atom into the meso-position of the external chain is slightly less than for methyl. The cyano group in this position slightly increases the color (by 6 nm). Phenyl and methyl groups in the 8-position of these dyes cause a bathochromic shift of the absorption maximum. A considerable bathochromic shift (38 nm) is seen in the case of 2,2'-diphenyl-8,10-dimethylindolo-3,3'-trimethinecyanine, i.e., following the introduction of methyl groups simultaneously into the 8- and 10-positions.

The relationship observed between the structures and colors of these dyes is apparently to be explained as follows. Quantum-chemical calculations show that trimethinecyanines which are derived from 1-alky1- and 1-alky1-2-arylindoles, in the ground and excited singlet states, are characterized by a less even distribution of electron density along the polymethine chromophore, and lower values at the carbon atoms of the external chain, than in the thiacarbocyanines; the 3,3'-carbon atoms of the indole hetero-residues and $C_{(9)}$ of the external chain carry a negative charge, and the positive charge is localized accordingly on $C_{(2)}$, $C_{(2')}$, $C_{(8)}$, and $C_{(10)}$ of the chromophore of (I). A chlorine atom in the mesoposition of the external chain results in an increase in the evenness of distribution of electron density along the chromophore, and accordingly to a bathochromic shift in the absorption maximum. However, the spatial structure of trimethinecyanines (I) substituted in the meso-position of the polymethine chain, from a consideration of Stuart-Briegleb models, cannot be completely planar. In the cases of the 9-methyl (chloro, bromo, and cyano) derivatives, there is a greater or lesser departure of the substituents, and/or the terminal hetero-residues, at a slight angle to the planar arrangement, which is apparently responsible for the differences in their colors. A phenyl group in the 8-position in the cyanines (I) evidently promotes greater delocalization of the charges on the atoms of the chromophore than in the unsubstituted dye, since in this case it is possible for it to be disposed in a plane parallel to the plane of the phenyl group in the 2-position of the indole hetero-residue (perpendicular to the plane of the chromophore). A methyl group in the 8-position and/or the 10-position also appears to increase the delocalization of electron density in the chromophore, since it is less likely to have a steric effect in these positions.

The data presented in Table 1 show that dyes (Ie, o, q, r), which contain an alkyl or aryl group in the 8-position of the external chain, have somewhat greater values of the polarographic reduction potentials than the corresponding unsubstituted cyanines (Ia, f). The introduction of a halogen atom into the p-position of the 2-aryl group of the indole hetero-residue results in a decrease in the reduction potential (cf. dyes Io, q). A methoxygroup in the p-position of the 8-phenyl group has the opposite effect.

An examination of the photographic properties of these dyes showed that 8-arylsubstituted 2,2'-diarylindolo-3,3'-trimethinecyanines are efficient sensitizers for direct positive photographic emulsions in the spectral region 580-780 nm. They are all efficient electron acceptors. Their high photographic efficiency is in accordance with their polarographic reduction potentials (Table 1). Some of the 2,2',8-triarylindolo-3,3'-trimethinecyanines are readily and completely decolorized following photographic treatment, and they have interesting anti-halo properties.

EXPERIMENTAL

The spectra of the dyes were obtained on an SF-10 spectrometer, and mass spectra on a Varian MAT-311 A instrument, ionizing potential 70 eV, cathode emission current 300 μ A, accelerating voltage 3 kV.

<u>8- and 9-Methylindolo-3,3'-trimethinecyanines (Ib, g, h, o).</u> To a solution of 0.01 mole of 1-methyl-2-R¹-indole in 15 ml of dry benzene was added 0.005 mole of 1,1,3,3-tetraethoxy-butane or 2-methyl-1,1,3,3-tetraethoxypropane [4]. We then added dropwise, with stirring at ambient temperature, a solution of 0.01 mole of acetyl chloride in 5 ml of benzene, over 30 min. The mixture was kept for 17 h at ambient temperature, and the solid was filtered off, washed with dry benzene and ether, and dried over calcium chloride. The dyes were purified by recrystallization from methanol in the presence of hydrochloric or perchloric acid. The properties of the dyes and the analytical data are given in Table 2.

<u>1,1',8,10-Tetramethyl-2,2'-diphenylindolo-3,3'-trimethinecyanine Perchlorate (In)</u>. To a solution of 0.01 mole of (II) in 35 ml of acetic anhydride was added 0.04 mole of acetylacetone. TSA (0.01 mole) was then added portionwise at ambient temperature over 1 h with stirring. After 1 h 30 min, the mixture was poured into 600 ml of ice water and 15 ml of 70% perchloric acid. On the following day, the solid was filtered off, washed with dry benzene and ether, and dried *in vacuo* over calcium chloride. The dye was purified by repricipation from a solution in acetic anhydride with benzene in the presence of TSA.

<u>1,1-Dimethyl-2,2',8-triarylindolo-3,3'-trimethinecyanines (Ie, o-r)</u>. To a solution of 0.01 mole of the substituted indole in 20-30 ml of acetic anhydride was added 0.005 mole of the aroylacetaldehyde diethyl acetal (or its anil). A solution of 0.01 mole of TSA in 10 ml of acetic anhydride was then added over 30 min, with stirring at ambient temperature. After 2-3 h, the mixture was poured into a solution of TSA in 1 liter of dry ether. After 12 h, the solid was filtered off, washed with dry ether, and dried *in vacuo*. The bromides and iodides of dyes (Ie, p, q, r) were obtained by heating their alcoholic solutions for 3 min with an equal volume of a 10% aqueous solution of potassium bromide or iodide, and were purified by recrystallization from ethanol in the presence of the appropriate mineral acid (Table 2).

<u>l-Methyl-2-phenyl-3-(2'-cyano-2'-formylvinyl)indole (III)</u> was obtained by condensing 1 mole of (II) with 1 mole of 2-cyano-3-dimethylaminoacrolein in benzene in the presence of 1 mole of acetyl chloride at 20°C for 2 h. Yields 15-20%. Yellow plates (from ethanol), mp 240-241°C. IR spectrum: 2220 (C=N), 1680 (>CO), 1570 cm⁻¹ (>C=C< of the substituent in the

TABLE 2. Properties of Indolo-3,3'-trimethinecyanines (I)

Com-	Mp, °C	Found, %			Molecular	Calculated, %			Yield,	
pound	(decomp.)	С	н	N	formula	с	н	N	%	
Ib Ie Ig Ih Im In Io Ip Iq Ir Is	120-121a 156-157b 180-181c 158-160b 159-160a 169-170d 134-135c 214-215c 211-212c 184-185c 231-232e	76,4 65,4 81,3 61,8 72,0 73,0 79,0 77,35 61,15 75,3 70,7	$\begin{array}{c} 6,75\\ 5,0\\ 5,9\\ 4,0\\ 5,1\\ 5,1\\ 5,5\\ 5,6\\ 3,8\\ 5,2\\ 4,8\end{array}$	7,2 5,2 5,3 4,1 4,8 4,6 4,0 4,4 3,6 4,4	$\begin{array}{c} C_{24}H_{25}ClN_2\\ C_{29}H_{27}IN_2\\ C_{34}H_{29}ClN_2\\ C_{34}H_{29}ClN_2O_4\\ C_{35}H_{31}ClN_2O_4\\ C_{35}H_{31}ClN_2O_4\\ C_{46}H_{38}N_2O_3S\\ C_{41}H_{35}BrN_2\\ C_{39}H_{29}Br_3N_2\\ C_{40}H_{33}BrN_2O\\ C_{34}H_{26}ClN_3O_4^{\rm c}\end{array}$	$\begin{array}{c} 76,5\\ 65,6\\ 81,5\\ 62,0\\ 72,3\\ 73,15\\ 79,1\\ 77,5\\ 61,2\\ 75,35\\ 70,9 \end{array}$	$\begin{array}{c} 6,7\\ 5,1\\ 5,8\\ 4,1\\ 5,2\\ 5,3\\ 5,5\\ 5,55\\ 3,8\\ 5,2\\ 4,6\end{array}$	7,4 5,3 5,6 4,25 4,95 4,7 4,0 4,4 3,7 4,4	$\begin{array}{c} 44\\ 52\\ 10\\ 10\\ 14\\ 30\\ 74\\ 71\\ 29\\ 41\\ 40\\ \end{array}$	

^aViolet prisms. ^bDeep violet prisms. ^cGreen prisms, ^dDeep blue prisms. ^eDark green prisms. ^fFound, %: Cl 5.9. Calculated, %: Cl 6.1.

TABLE 3. Mass Spectra of Indolocyanines and Their Derivatives

Compound	m/z values (as % of the maximum peak)							
111	57,2 (25,34), 69,2 (6,19), 71,3 (10,36), 77,2 (5,43), 128,1 (5,18), 206,2 (15,11), 207,2 (100,00), 208,2 (16,96), 214,1 (7,24), 218,2 (7,29), 241,1 (11,08), 242,1 (25,85), 243,1 (6,07), 255,2 (7,37), 256,2 (8,69), 257,2 (30,73), 258,2 (16,15), 286,2 (78,24)							
I,e	57,1 (10,73), 72,6 (8,96), 77,1 (51,44), 105,1 (44,18), 120,1 (15,22), 126,9 (36,53), 144,0 (98,24), 145,0 (100,00), 146,1 (11,02), 170,1 (7,39), 231,0 (9,58), 232,0 (9,80), 246,1 (11,64), 247,1 (14,16), 253,8 (68,88), 257,1 (28,87)							
I o (bromide)	57,1 (5,86), 79,0 (12,01), 80,0 (30,60), 81,0 (11,59), 82,0 (30,86), 207,1 (10,38), 218,1 (24,95), 219,1 (8,27), 220,1 (35,94), 221,1 (8,54), 244,1 (11,06), 263,1 (21,17), 263,6 (12,79), 264,1 (11,32), 264,6 (4,33), 294,0 (15,81), 295,0 (24,44), 296,0 (13,92), 304,0 (10,38), 307,1 (7,44), 308,1 (12,03), 318,1 (30,67), 319,1 (18,27), 320,1 (18,91), 321,1 (10,39), 449,0 (33,94), 350,1 (12,37), 451,0 (15,12), 525,1 (24,69), 526,1 (100,00), 527,0 (70,74), 528,0 (49,02), 529,1 (17,73)							
Ir	79,0 (65,74), 80,0 (76,22), 81,0 (58,54), 82,0 (75,84), 91,0 (42,11), 92,0 (23,90), 93,0 (97,08), 94,0 (100,00), 94,9 (78,59), 96,0 (100,00), 97,0 (5,97), 206,1 (15,90), 207,1 (41,82), 208,1 (7,11), 278,1 (7,09), 556,0 (30,70), 557,0 (13,87), 558,0 (5,74)							

3-position). Found, %: C 79.6; H 4.95; N 9.85. $C_{19}H_{14}N_2O$. Calculated, %: C 79.6; H 4.9; N 9.8.

1,1-Dimethy1-2,2'-dipheny1-9-cyanoindolo-3,3'-trimethinecyanine perchlorate (IV) was obtained by reacting 0.01 mole of (III) with 0.01 mole of (II) in nitromethane at 20°C, in the presence of 0.01 mole of TSA, followed by conversion of the tosylate into the perchlorate in the usual way.

<u>1,3-Bis-(1-methyl-2-phenyl-3-indolyl)-2-phenylazo-3-hydroxy-1-propene (IVa)</u>. A mixture of 0.01 mole of (II), 0.005 mole of 2-phenylazomalondialdehyde, and 0.005 mole of TSA was triturated, and 10 ml of acetic anhydride added (exothermic reaction). After 10 min, the mixture was poured into 800 ml of water; the oily precipitate, which crystallized, was filtered off, washed with water until neutral, and twice recrystallized from ethanol to give 20% of red prisms (from ethanol), mp 155-156°C, absorption maximum (in ethanol) 440 nm, $\lambda_{max} 6.75 \cdot 10^3$. Found, %: C 81.55; H 5.6; N 9.35. C₃₉H₃₂N₄O. Calculated, %: C 81.8; H 5.6; N 9.7.

<u>1,3-Bis-(1-methyl-2-phenylindol-3-yl)-2-nitro-3-hydroxy-1-propene (IVb)</u>. To a solution of 0.01 mole of (II) in 75 ml of acetic acid was added 0.005 mole of the sodium salt of nitromalondialdehyde, the mixture stirred for 10 min, and 0.01 mole of TSA added with stirring in small portions at ambient temperature. After 1 h, the solid was filtered off and twice recrystallized from benzene. Yield, 25%. Orange prisms (from ethanol), mp 267-268°C, absorption maximum (in ethanol), 445 nm. Found, %: C 77.05; H 5.5; N 8.05. C_{33H27}N₃O₃.

Calculated, %: C 77.2; H 5.3; N 8.2.

The mass spectra contained ion peaks corresponding to the molecular masses of the ions $[M - HX]^+$. Ion peaks were present with m/z 94:96, confirming the presence of the methyl group on the indole nitrogen atom, and an ion with m/z 207, corresponding to the structure of the substituted indole residue (1-methyl-2-phenylindole, etc.), and fragment ions indicating the presence of a phenyl group in the o-position, in accordance with the process $[M - HX]^+ - C_6H_5$.

LITERATURE CITED

- 1. P. I. Abramenko, T. N. Galiullina, and A. N. Gusarov, in: Collected Scientific Papers of the GosNIIkhimfotoproekt [in Russian], Moscow (1980), p. 126.
- 2. T. N. Galiullina, P. I. Abramenko, A. V. Kazymov, and V. M. Gorokhovskii, Khim. Geterotsikl. Soedin., No. 8, 1067 (1981).
- 3. T. N. Galiullina, P. I. Abramenko, and V. K. Kalent'ev, in: Collected Scientific Papers of the GosNIIkhimfotoproekt., Moscow (1981), p. 46.
- 4. A. A. Yanovskaya, S. S. Yufit, and V. F. Kucherov, Izv. Akad. Nauk SSSR, Otdel Khim. Nauk, 2184 (1960).

INTERACTION OF 3-ARYLIDENAMINOCARBAZOLES WITH ANTIPYRINE

V. I. Letunov, T. P. Shulyat'eva, UDC 547.838.1'751'773'774'759.3.07:543.422'51 and V. V. Misenzhnikov

The interaction of 3-arylidenaminocarbazoles with antipyrine in the presence of catalytic amounts of acid leads to the formation of derivatives of [3,2-f]-pyrazolo[4,3-c]quinoline.

Methyl ketones are added at the azomethine bond in the reaction with 3-arylidenaminocarbazoles in the presence of acid. The arylaminoketones formed in this case are cyclized to derivatives of 7H-pyrido[2,3-c]carbazole [1]. In this work antipyrine was used instead of methyl ketone.

Antipyrine was studied previously in reactions with Schiff bases, produced from amines of the benzene series. It was found in this case that it forms addition products at the azomethine bond without their subsequent cyclization [2, 3]; however, as the present investigation showed, antipyrine forms cyclic products with 3-arylidenaminocarbazoles derivatives of indolo[3,2-f]pyrazolo[4,3-c]quinoline, which undergo supplementary transformations in the course of the reaction, as can be represented by the following scheme:



Fig. 1. UV spectra (in methanol): 1) 3-m-chlorobenzylidenaminocarbazole (Id); 2) condensation product of 3-m-chlorobenzylidenaminocarbazole with antipyrine (IIId); 3) condensation product of benzylidene-3-aminocarbazole with antipyrine (IIIa).

N. G. Chernyshevskii Chita State Pedagogical Institute, Chita 672033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1657-1659, December, 1983. Original article submitted February 3, 1983.