2. Organic Syntheses [Russian translation], Collective Vol. 1, Izv. Akad. Nauk SSSR, Moscow (1950), p. 120.
3. R. Petit and R. Pallaud, Compt. Rend., 258, 230 (1964).
4. K. G. Lewis and C. R. Malqiney, Tetrahedron, 33, 463 (1977).
5. I. S. Barvinok and V. S. Kuprin, Z h. Obshch. Khim., 31, 632 (1961).

SYNTHESIS AND PROPERTIES OF SUBSTITUTED INDOLO-3-CYANINE DYES

T. N. Galiullina, P. I. Abramenko,
A. V. Kazymov, and V. M. Gorokhovskii

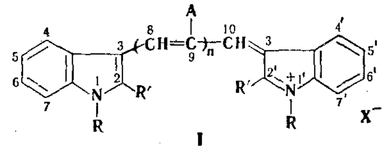
UDC 668.819.45'547.759.07

Indolo-3,3'-mono- and indolo-3,3'-trimethylidynecyanines that contain substituents in the indole rings and in the polymethine chain (in the case of trimethylidynecyanines) were synthesized by condensation of 2-alkyl- and 2-arylindoles, respectively, with ethyl orthoformate and tetraalkylacetals of substituted malonic dialdehydes in anhydrous benzene in the presence of acetyl chloride or thionyl chloride. The colors of the products were studied, and the polarographic potentials of the oxidation and reduction half waves were determined. A relationship between the indicated characteristics of indolo-3-cyanines and their structure was established.

Cyanine dyes that are derivatives of 2-arylindiles occupy an important position among spectral sensitizers of silver halide photographic emulsions [1, 2]. These compounds are effective electron acceptors and are suitable for use in direct positive photomaterials.

In this connection, we decided to synthesize new substituted (in the indole ring and in the polymethine chain) indolo-3,3'-cyanine dyes, to study their colors and sensitizing action, to determine the polarographic potentials of the oxidation and reduction half waves, and to establish a relationship between the indicated characteristics of these dyes and their structure.

With this in mind we synthesized symmetrical indolo-3,3'-cyanines with the general structure (I)



I

R=H or CH_3, R'=CH_3, C_6H_5 or Ar, A=H or Hal, n=0 or 1, X^- — acid residue

Indolo-3-monomethylidynecyanines (n = 0) were obtained by condensation of the corresponding 2-arylindoles with ethyl orthoformate in anhydrous benzene at room temperature [3]. Symmetrical indolo-3-trimethylidynecyanines (n = 1) were synthesized by condensation of 2-alkyl- and 2-arylindoles with tetraalkylacetals of malonic dialdehydes in anhydrous benzene in the presence of thionyl chloride or acetyl chloride at room temperature [4].

The spectral and redox characteristics of the synthesized dyes in a mixture (5:1) of nitromethane and acetic acid are presented in Table 1. The data in Table 1 show that the colors of the indolo-3,3'-cyanines depend to an appreciable extent on the character and position of the substituents in the indole heteroresidues and the polymethine chain. Replacement of the hydrogen atom attached to the indole nitrogen atom of 2-phenylindole by a methyl group leads to a hypsochromic shift of the absorption maximum. The dyes that contain phenyl groups in the 2 and 2' positions of the indole residues are considerably more deeply

---

Kazan Scientific-Research Institute of Technology and Design of the Photographic Chemical Industry, Kazan 420035. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1067-1071, August, 1971. Original article submitted October 28, 1980.

0009-3122/81/1708-0790$07.50

TABLE 1. Spectral and Polarographic Characteristics of Dyes with the I Structure*

Compound	In formula I					λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	$E_{1/2}^{ox}$†	$E_{1/2}^{red}$‡	ΣE
	R	R′	A	n	X					
Ia	CH_3	CH_3	H	0	Cl	495	6,75	0,72	−0,70	+0,02
Ib	CH_3	CH_3	H	1	Cl	568	13,25	1,17	−0,41	+0,76
Ic	CH_3	CH_3	Cl	1	Cl	592	11,5	0,66	−0,93	−0,27
Id	CH_3	CH_3	Br	1	Cl	568	14,5	0,38	−0,48	−0,10
Ie	H	C_6H_5	H	0	Br	534	4,0	0,74	−0,57	+0,17
If	H	C_6H_5	H	1	Cl	596	11,4	1,17	−0,41	+0,76
Ig	CH_3	C_6H_5	H	0	Br	520	4,5	0,84	−0,60	+0,24
Ih	CH_3	C_6H_5	H	1	Cl	592	10,0	1,14**	−0,26	+0,88
Ii	CH_3	C_6H_5	Cl	1	Cl	610	4,7	1,12	−0,21	+0,91
Ij	CH_3	C_6H_5	Br	1	Cl	592	10,0	1,18 1,17**	−0,24	+0,94 +0,93
Ik	CH_3	p-$CH_3C_6H_4$	H	1	Cl	592	13,75	0,60	−0,29	+0,31
I*l*	CH_3	p-$CH_3C_6H_4$	Br	1	Cl	595	10,6	0,63	−0,26	+0,37
Im	CH_3	p-$CH_3OC_6H_4$	H	1	Cl	598	10,25	1,11	−0,36	+0,75
In	CH_3	p-$CH_3OC_6H_4$	Br	1	Cl	598	9,62	1,10	−0,40	+0,70
Io	CH_3	p-BrC_6H_4	H	1	Cl	594	12,25	1,14	−0,22	+0,92
Ip	CH_3	p-BrC_6H_4	Br	1	Cl	598	10,62	1,05	−0,25	+0,80

---

*Obtained by S. Kh. Krut' and I. S. Koretskaya. †With a glass–graphite electrode. ‡With a dropping mercury electrode. **With an H·Pt electrode.

TABLE 2. Charges (q_r) and Bond Orders (P_{rs}) of Dyes I in the Ground ($^1S_0$) and Excited ($^1S_1$) Singlet States

Compound	$^1S_0$ state								
	q_r					p_{rs}			
	N_1	C_2	C_3	C_8	C_9	1—2	2—3	3—8	8—9
Ib	0,306	0,108	−0,084	0,210	−0,046	0,516	0,652	0,536	0,656
Ih	0,288	0,101	−0,083	0,180	−0,048	0,481	0,612	0,555	0,655
Im	0,281	0,101	−0,088	0,167	−0,059	0,473	0,605	0,561	0,654
Ic	0,301	0,086	−0,078	0,202	−0,037	0,508	0,658	0,537	0,641
Iq*	0,288	0,099	−0,082	0,180	−0,048	0,481	0,611	0,555	0,655
	$^1S_1$ state								
Ib	0,314	0,051	0,009	−0,069	0,071	0,501	0,602	0,508	0,629
Ih	0,277	0,045	0,022	−0,066	0,078	0,456	0,556	0,533	0,630
Im	0,261	0,026	0,007	−0,063	0,057	0,434	0,563	0,537	0,634
Ic	0,320	0,029	0,009	−0,074	0,078	0,505	0,611	0,516	0,602
Iq*	0,277	0,044	0,022	−0,061	0,077	0,456	0,555	0,535	0,630

---

*For Iq: R = CH_3 and R^1 = C_6H_4CN-p.

colored than the corresponding methyl-substituted cyanines; this is due to the more uniform distribution of the electron density (and the greater uniformity of the bond orders) between the atoms of the polymethine chromophore in the 2,2'-diphenyl derivatives (Table 2) in the ground ($^1S_0$) and excited ($^1S_1$) singlet states. The incorporation of electron-donor substituents in the para positions of the phenyl groups in 2,2'-diphenylindolo-3,3'-cyanines leads to an increase in the uniformity of the distribution of the electron density in the chromophore and, as a consequence of this, to further deepening of the color. The results of quantum-chemical calculations (Table 2) show that the introduction of electron-acceptor substituents in the same positions of the phenyl groups should also have the same effect. A chlorine atom in the meso position of the polymethine chain of cyanines I also leads to a considerable increase in the uniformity of the distribution of the electron density along the conjugated polymethine chain and, in conformity with this, to a bathochromic shift of their absorption maxima. At the same time, a bromine atom in the same position of the polymethine chain of dyes I has virtually no effect on their color; this is evidently due to the steric effect in connection with its greater atomic radius than in the case of the chlorine atom.

It has been previously shown [5, 6] that indolo-3-cyanines, the overall oxidation ($E_{1/2}^{ox}$) and reduction ($E_{1/2}^{red}$) half-wave potentials of which have positive values, are effective electron acceptors that are recommended for use in direct positive photomaterials.

It follows from the data in Table 1 that the sums of the oxidation and reduction half-wave potentials of almost all of the investigated indolo-3,3'-mono- and trimethylidynecyanines are positive. Consequently, all of them are suitable for spectral sensitization (as electron acceptors) of direct positive photoemulsions, particularly monodispersed fogged emulsions with fog centers on the surface of silver halide grains. This is particularly characteristic for the synthesized 1-alkyl-2-arylindolo-3-trimethylidynecyanines. A shift (of ∿0.15 V) of the reduction half-wave potentials to the anode region is observed when aromatic groups are introduced in the 2 and 2' positions of indolo-3,3'-trimethylidynecyanines. Halogen atoms (chlorine and bromine) in the meso position of the polymethine chain have a less significant effect.

2-(p-Methoxyphenyl)indolo-3,3'-trimethylidynecyanines have reduction half-wave potentials that are shifted to the cathode region, while dyes with bromine atoms in the same positions of the 2,2'-phenyl groups have reduction half-wave potentials that are shifted to the anode region (as compared with unsubstituted 2,2'-diphenylindolotrimethylidynecyanines); this is in agreement with the electron-donor and electron-acceptor effect of the methoxy group and bromine atoms, respectively. The oxidation and reduction half-wave potentials are shifted (∿0.3-0.4 V) to the anode region on passing from indolo-3,3'-monomethylidynecyanines to indolo-3,3'-trimethylidynecyanines, i.e., when the polymethine chain is made one vinylene group longer; this is similar to the change in the corresponding characteristics of imidazo[4,5-b]quinoxalinomono- and trimethylidynecyanines [7], which are also recommended in a number of patents [8] as electron acceptors that spectrally sensitize direct positive photoemulsions. Thus quite distinct relationships exist between the polarographic characteristics and the structure of the investigated dyes. The synthesized trimethylidynecyanines sensitize photoemulsions to the region of the spectrum with a maximum mainly at 580-650 nm.

EXPERIMENTAL

The absorption spectra of the dyes in a mixture (5:1) of nitromethane and acetic acid were measured with an SF-10 spectrophotometer.

The polarographic studies were carried out with an LP-7 dc polarograph (Czechoslovak SSR). The cathode polarograms were recorded with a dropping mercury electrode and a Mairanovskii closed polarographic cell [9]. The air was removed from the solutions with a stream of purified nitrogen. A stationary graphite disk electrode prepared from spectrally pure graphite impregnated (*in vacuo*) with a mixture of paraffin and low-pressure polyethylene [10] was used as the indicator electrode for recording the anode polarograms. A saturated calomel electrode was used as the reference electrode for recording both the cathode and anode polarograms. Methanol and purified (by the method in [11]) acetonitrile were used to prepare the solutions of the dyes (with concentrations ranging from 10^{-4} to 10^{-3} mole/liter). A mixture of 0.05 mole/liter of sodium acetate and 0.005 mole/liter of acetic acid in methanol served as the inert electrolyte during recording of the oxidation waves. A 0.05 mole/liter solution of lithium chloride in methanol or a solution of 0.01 mole/liter of lithium perchlorate in acetonitrile served as the inert electrolyte during recording of the reduction waves.

2-Phenyl- and 1-methyl-2-(p-methoxyphenyl)indole were obtained in 70-75% yields by the action of, respectively, phosphoric acid on acetophenone phenylhydrazone [12] and polyphosphoric acid on p-methoxyacetophenone α-methylphenylhydrazone [13] with heating. 1-Methyl-2-phenylindole [14], 1,2-dimethylindole [15], and 1-methyl-2-(p-tolyl)indole [13] were synthesized in 60-89% yields by methylation of the corresponding N-unsubstituted indoles with dimethyl sulfate in an alkaline medium. 1,1,3,3-Tetraethoxy-2-chloropropane [16] was obtained in 40% yield by chlorination of 1,1,3,3-tetraethoxypropane.

Indolo-3,3'-monomethylidynecyanines. A 0.005-mole sample of ethyl orthoformate and a solution of 0.4 ml of thionyl chloride in 5 ml of anhydrous benzene were added with stirring at room temperature to a solution of 0.01 mole of substituted indole in 10 ml of anhydrous benzene, and the mixture was maintained at room temperature for 17 h. The precipitate was removed by filtration, washed with anhydrous benzene and anhydrous ether, and air dried.

TABLE 3. Characteristics of Ia-p

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
Ia	93–95	67,6	6,9	7,6	$C_{21}H_{21}ClN_2 \cdot 2H_2O$	67,6	6,8	7,5	65
Ib	195–196	68,0	7,0	6,7	$C_{23}H_{23}ClN_2 \cdot 2{,}5H_2O$	68,2	7,0	6,9	62
Ic	148–150	62,4	6,1	6,4	$C_{23}H_{22}Cl_2N_2 \cdot 2{,}5H_2O$	62,4	6,2	6,3	66
Id	171–172	58,3	6,1	5,5	$C_{23}H_{22}BrClN_2 \cdot C_2H_5OH \cdot 1{,}5H_2O$	58,3	6,1	5,4	20
Ie	240–241	70,9	5,2	5,4	$C_{29}H_{21}BrN_2 \cdot C_2H_5OH$	71,1	5,2	5,35	52
If	265–266	81,3	5,0	6,1	$C_{31}H_{23}ClN_2$	81,1	5,0	6,1	73
Ig	174–175	73,6	5,0	5,5	$C_{31}H_{25}BrN_2$	73,6	5,0	5,5	42
Ih	213–214	81,4	5,6	5,7	$C_{33}H_{27}ClN_2$	81,4	5,6	5,7	81
Ii	224–225	67,7	4,4	4,9	$C_{33}H_{26}Cl_2N_2O_4$	67,7	4,4	4,8	51
Ij	219–220	70,2	4,8	5,1	$C_{33}H_{26}BrClN_2$	70,1	4,6	5,0	14
Ik	200–201	78,8	5,94	4,94	$C_{35}H_{31}ClN_2 \cdot H_2O$	78,8	6,2	5,2	78
Il	207–208	67,7	5,2	4,4	$C_{33}H_{30}BrClN_2 \cdot 1{,}5H_2O$	67,7	5,3	4,5	7
Im	177–178	73,3	6,9	4,4	$C_{35}H_{31}ClN_2O_2 \cdot 2C_2H_5OH$	73,3	6,8	4,4	35
In	201–203	59,9	5,1	3,5	$C_{35}H_{30}BrClN_2O_2 \cdot 2CH_3COOH \cdot 2H_2O$	59,9	5,4	3,5	35
Io	224–225	58,8	4,2	4,1	$C_{33}H_{25}Br_2ClN_2 \cdot 1{,}5H_2O$	58,9	4,2	4,1	39
Ip	236–237	54,7	3,3	3,8	$C_{33}H_{24}Br_3ClN_2$	54,8	3,3	3,8	67

The dyes were purified by reprecipitation from ethanol by the addition of ether, by chromatography on L 100/250 silica gel, and by recrystallization from ethanol. The chlorides of the dyes were converted to the bromides by heating alcohol solutions of them in a mixture with an equal volume of a 10% solution of potassium bromide. Bromide Ie (Table 3) was obtained by refluxing the chloride in a mixture (1:3) of 48% hydrobromic acid and ethanol for 5-10 min.

Indolo-3,3'-trimethylidynecyanines. These compounds were obtained by condensation of the corresponding substituted indole with 0.005 mole of unsubstituted or substituted tetraethoxypropane in anhydrous benzene in the presence of 0.005 mole of thionyl chloride or acetyl chloride at room temperature for 17-170 h. The dyes were purified by chromatography on L 100/250 silica gel and by recrystallization from ethanol or acetic acid.

The characteristics of all of the dyes and the results of analysis are presented in Table 3.

The quantitative determination of the percentages of water and solvents in the dyes was carried out by gas–liquid chromatography (GLC) with a Khrom-3 chromatograph with a thermal conductivity detector [the carrier gas was helium, and the adsorbents were Polysorb-1 or Porapak Q (0.16-0.20 mm fraction) (USA)] at a vaporizer temperature of 150°C.

The quantum-chemical calculations of the indolo-3,3'-trimethylidynecyanines were performed by the self-consistent-field (SCF) MO method within the Pariser–Parr–Pople (PPP) approximation with the aid of the program in [17] and the parameters from [18, 19].

LITERATURE CITED

1. J. Götze, West German Patent Application No. 1547643 (April 7, 1974); Izobret. Rubezhom, No. 13, 80 (1974).
2. D. D. Chapman, U. S. Patent No. 3598596; Ref. Zh. Khim., 10N630 (1972).
3. W. König, J. Prakt. Khim., 84, 214 (1911).
4. T. G. Gnevysheva, USSR Inventor's Certificate No. 342874; Byull. Izobret., No. 20 (1972).
5. Agfa-Gevaert, U.S. Patent No. 3957518; Izobret. Rubezhom, No. 17, 41 (1976).
6. P. B. Gilman and J. V. Morgan, US Patent No. 4011081; Ref. Zh. Khim., 24N260 (1977).
7. R. O. Loutfy and J. H. Sharp, Phot. Eng., No. 4, 165 (1976).
8. V. K. Kalent'ev, T. N. Galiullina, N. N. Sazonova, T. K. Sartakova, A. S. Granina, N. A. Stenina, and M. I. Stenina, Direct Positive Photographic Materials. Catalog of Bibliographies of the State Public Scientific and Technical Library of the USSR [in Russian], No. 12 (1977).
9. S. G. Mairanovskii, Ya. P. Stradyn', and V. D. Bezuglyi, Polarography in Organic Chemistry [in Russian], Khimiya, Moscow (1975), p. 325.
10. Kh. Z. Brainina, Inversion Voltammetry of Solid Phases [in Russian], Khimiya, Moscow (1972).
11. A. Weissberger and E. Proskauer, Organic Solvents, Wiley (1958).

12. N. I. Grineva, V. L. Sadkovskaya, and V. N. Ufimtsev, Zh. Obshch. Khim., 33, 552 (1963).
13. G. J. Gale, J. Lin, and J. F. K. Wilshire, Aust. J. Chem., 29, 2747 (1976).
14. V. I. Shvedov, G. N. Kurilo, and A. N. Grinev, Khim.-farm. Zh., No. 3, 11 (1970).
15. J. Degen, Lieb. Ann., 236, 151 (1886).
16. T. V. Protopopova and A. P. Skoldinov, Zh. Obshch. Khim., 29, 3928 (1959).
17. V. A. Kosobutskii, Master's Dissertation, Rostov-on-Don (1974).
18. P. I. Abramenko and V. A. Kosobutskii, Khim. Geterotsikl. Soedin., No. 5, 626 (1978).
19. P. I. Abramenko, A. N. Gusarov, and V. A. Kosobutskii, Zh. Prikl. Spektrosk., 31, 91 (1979).

REACTION OF METHIODIDES OF 1,2,3,4-TETRAHYDRO-γ-CARBOLINES WITH NUCLEOPHILIC AGENTS

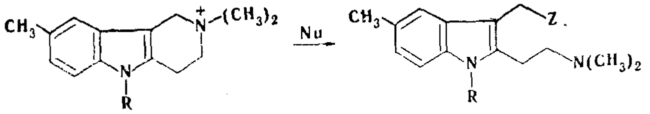
M. A. Yurovskaya and I. L. Rodionov

UDC 547.752:754'759.3:543.51

It is shown that C, N, and O nucleophiles smoothly cleave the hydrogenated ring of quaternized tetrahydro-γ-carbolines to give isotryptamine derivatives with a CH_2Z substituent in the 3 position (Z = Me, Ph, CN, OEt, piperidino, and morpholino). The principles of the mass-spectral fragmentation of the synthesized compounds as a function of the character of the substituent attached to the methylene group in the 3 position were established.

The reaction of gramine (3-dimethylaminomethylindole) and its quaternary salts with nucleophilic agents, which leads to the most diverse indole derivatives, is widely known (for example, see [1]). Tetrahydro-γ-carbolines are cyclic analogs of gramines. Their reaction with nucleophilic agents should lead to opening of the hydrogenated ring to give isotryptamine derivatives that are difficult to obtain by other methods. However, the literature contains only individual patent data on the cleavage of the quaternized tetrahydro-γ-carboline system under the influence of thiolate ions [2, 3] and some C anions [4].

In the present research we investigated the reaction of 3,6-dimethyl- (Ia) and 3,6,9-trimethyl-1,2,3,4-tetrahydro-γ-carboline methiodide (Ib) with C, N, and O nucleophiles. We selected the readily accessible 3,6-dimethyl-1,2,3,4-tetrahydro-γ-carboline (IIIa) as the principal starting model.



I a, b

II a-g

I a $R=H$, b $R=CH_3$; II a-f $R=H$, g $R=CH_3$; II a $Nu=CH_3MgI$, $Z=CH_3$; b $Nu=C_6H_5MgBr$, $Z=C_6H_5$; c $Nu=CN^-$, $Z=CN$; d $Nu=OC_2H_5^-$, $Z=OC_2H_5$; e Nu= piperidine, Z=piperidino ; f, g Nu=morpholine, Z = morpholino

The methylation of carboline IIIa at the indole nitrogen atom was accomplished by the action of equimolar amounts of sodium hydride and methyl iodide in dimethyl sulfoxide (DMSO). The low yields (25-30%) of N-methylated IIIb in this case are evidently due to competitive quaternization of both carbolines to give their methiodides.

In contrast to the methods described in the literature for the preparation of quaternary salts of gramine, which are accompanied by side processes or give the products in low yields [5], we carried out the quaternization of carbolines IIIa, b with a 2.5-fold excess of methyl iodide in benzene and obtained methiodides Ia, b in quantitative yields. Side

---

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1072-1078, August, 1981. Original article submitted October 10, 1980.

0009-3122/81/1708-0794$07.50