Russian Journal of Organic Chemistry, Vol. 40, No. 2, 2004, pp. 228–231. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 2, 2004, pp. 256–260.

Synthesis of Amphiphilic Thiatrimethinecyanines

N.A. Orlova, E.F. Kolchina, M.M. Shakirov, T.N. Gerasimova*, and V.V. Shelkovnikov

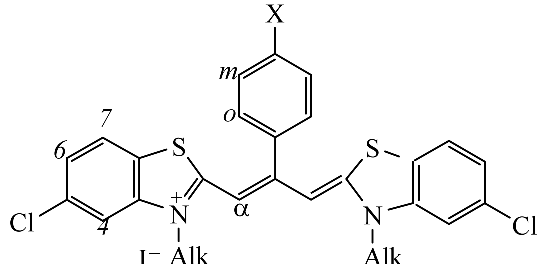
Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division,
Russian Academy of Sciences, Novosibirsk, 630090 Russia
fax: (3832) 344752 e-mail: vsh@nioch.nsc.ru

Received July 24, 2003

Abstract—Preparation conditions were optimized for 2-methyl-5-chlorobenzothiazolium quaternary salts with long-chain N-alkyl substituents ($C_{12}H_{25}$, $C_{15}H_{31}$, $C_{18}H_{37}$). They were used in the synthesis of thiatrimethinecyanines conteining in the *meso*-position phenyl, *p*-chlorophenyl, or *p*-fluorophenyl groups.

Organized molecular ensembles of organic compounds found application in the modern systems for information recording and processing [1]. An important place among them belongs to *J*-aggregates of polymethine dyes [2]. Recently high values of nonlinear cubic susceptibility were discovered in thin films of *J*-aggregates of 2,2'-quinomonomethinecyanines prepared without application of stabilizing polymers and without using Lengmuir–Blodgett technique [3]. The necessary condition of this aggregation is an amphiphilic character of the molecules imparted by long alkyl substituents at the heterocyclic nitrogen atoms. In order to get additional data on the effect of the dye structure on the aggregation and film-forming properties we undertook in this study a synthesis of amphiphilic thiatrimethinecyanines of a general formula **I**.

The presence in the molecule of dyes **I** of a trimethine chain results in the absorption shift to longer waves region compared to 2,2'-quinomonomethinecyanines [4], and the aryl substituents in the *meso*-position permit a variation of the electronic effect on the external polymethine chain. We selected as the initial heterocycle 5-chloro-



Ia–Ii

X = H, Alk = $C_{12}H_{21}$ (**a**), $C_{15}H_{31}$ (**b**), $C_{18}H_{37}$ (**c**); X = Cl, Alk = $C_{12}H_{21}$ (**d**), $C_{15}H_{31}$ (**e**), $C_{18}H_{37}$ (**f**); X = F, Alk = $C_{12}H_{21}$ (**g**), $C_{15}H_{31}$ (h), $C_{18}H_{37}$ (**i**).

substituted 2-methylbenzothiazole **II** for certain data existed [5] showing that the presence of chlorine in the 5,5'-positions of a thiamonomethinecyanine molecule favored the *J*-aggregation.

We formerly [6] showed the possibility of *J*-aggregation for dye **Ic** obtained in a low yield by N-alkylation of compound **II** with octadecyl *p*-chlorobenzenesulfonate followed by condensation of intermediately arising quaternary salt with trimethyl orthobenzoate by procedure [7]. In this study we performed the stage-by-stage investigation of the synthesis of dyes **I** using the high-resolution ^{1}H NMR spectroscopy as described in [4] for the preparation of amphiphilic 2,2'-quinomonomethinecyanines. The analysis of reaction mixtures obtained from compound **II** and *p*-chlorobenzenesulfonates synthesized by procedure [7] of general formula $C_nH_{2n+1}OSO_2C_6H_4Cl$-*p* [(**III**): $n = 12$ (**a**), $n = 15$ (**b**), $n = 18$ (**c**)] in the process carried out at 130–160°C (Table 1) demonstrated that the reaction proceeded similarly to that of 2-methyl-quinoline [4]. A typical composition of the reaction mixture obtained by heating benzothiazole **II** with sulfonic ester **III** is presented on the scheme.

In the reaction mixture besides quaternary salt **IV** were identified initial compounds **II** and **III**, 2-methyl-5-chlorobenzothiazole *p*-chlorobenzenesulfonate **V,** and also, as expected [4], the products of side transformations **VI** and **VII** of the initial sulfonic ester. The optimum composition of reaction mixtures in all cases was attained at 150°C, and the content of the target products **IVa–IVc** did not exceed 50%. It is presumable (cf. [4]) that the alkylation efficiency of initial heterocyclic compounds **II** is reduced by competing conversions of carbocations

1070-4280/04/4002-0228©2004 MAIK “Nauka/Interperiodica”

Table 1. Composition of reaction mixtures obtained in reaction of benzothiazole **II** with *p*-chlorobenzenesulfonates **IIIa–IIIc** (according to ^{1}H NMR data)[a] **II + IIIa–c→II + IIIa-c + IVa-c + V + VIa-c + VIIa-c**

Reaction temperature, °C	Content, %																	
	II			**IIIa–IIIc**			**IVa–IVc**			**V**			**VIa–VIc**			**VIIa–VIIc**		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
130	30	30	30	25	30	35	25	20	20	15	10	10	< 5	5	–	< 5	5	5
140	20	40	20	10	20	30	40	25	30	20	5	10	5	5	–	5	5	>5
150	5	5	20	5	–	20	50	45	35	30	30	10	5	>5	5	5	10	10
160[b]	–	–	15	–	–	25	50	40	35	30	30	15	5	5	< 5	10	10	10

[a] The data are given with an accuracy of 5%. The overall content of compounds listed in the Table is taken for 100%. The presence of unidentified impurities is not excluded. A signal with a chemical shift of ~5.4 ppm and multiplicity of additional signals suggest formation of alkenes (A) with an internal double bond; the mixture "b" may contain ~15% of alkene (A).

arising intermediately from sulfonic esters **III** under the reaction conditions.

Quaternary salts **IVa–IVc** were isolated in 26–39% yield by washing the mixtures in succession with ethyl ether and acetonitrile. Their composition and structure was proved by elemental analysis and ^{1}H NMR spectra.

Dyes **Ia–f** were prepared by boiling in pyridine salts **IVa–IVc** with trimethyl orthobenzoate, ortho(*p*-chlorobenzoate), and ortho(*p*-fluorobenzoate) **VIIIa–VIIIc** obtained from the corresponding benzotrichlorides [8]. Yields of the dyes after isolation from the mixture and purification attained 10–28%. We failed to increase the yield by carrying out the synthesis in DMSO instead of pyridine that had brought the success in [4]. The composition and structure of dyes was proved by elemental analysis and ^{1}H NMR spectra (Tables 2 and 3). Electron absorption spectra of the dyes in $CHCl_3$ are identical and virtually coincide with the spectrum of their *N,N'*-diethyl-substituted analog [9]. As should be expected [10], the length of N-alkyl group does not affect the dye absorption in the monomer state.

EXPERIMENTAL

^{1}H NMR spectra were recorded on spectrometers Bruker DRX-500 and AC-200 from solutions in $CDCl_3$. Chemical shifts are reported in the δ scale. Electron absorption spectra are registered on spectrophotometer HP-8453 from solutions in $CHCl_3$ (longwave absorption maxima are reported).

The column chromatography was performed on alumina of the II activity grade. For solvent mixtures used as eluents the volume ratios are given.

Synthesis of 2-methyl-3-alkyl-5-chlorobenzothiazolium *p*-chlorobenzenesulfonates (IVa–c). A mixture of 5 mmol of 2-methyl-5-chlorobenzothiazole **II** [11] and 5 mmol of the respective alkyl-*p*-chlorobenzenesulfonate **III** was heated for 5 h under conditions indicated in Table 1. The reaction mixtures were analyzed by ^{1}H NMR spectroscopy (cf. [4]). The composition of mixtures is ccompiled in Table 1.

On cooling the solidified reaction product was ground with Et_2O, the precipitate was filtered off and washed in

Scheme.

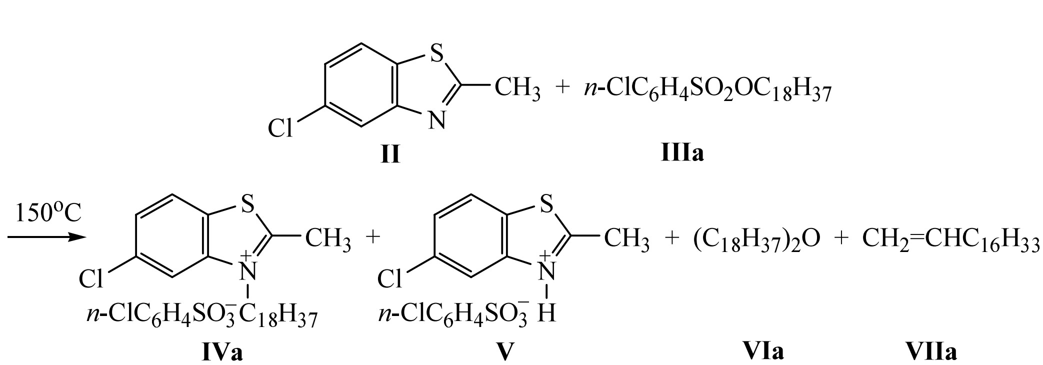


Table 2. Yields, melting points, electron absorption spectra, and elemental analyses of compounds **I–IV**

Compd. no.	Yield, %	mp (decomp), °C	Λ_{max}, nm (log ε)	Found, %					Formula	Calculated,%				
				C	H	I	N	S		C	H	I	N	S
Ia	10	225–227	546 sh (4.62), 584 (5.23)	61.50	6.96	13.75	2.60	6.92	$C_{47}H_{63}Cl_2IN_2S_2$	61.49	6.92	13.82	3.05	6.99
Ib	22	215–218	546 sh (4.68), 584 (5.31)	63.52	7.22	12.64	2.57	6.20	$C_{53}H_{75}Cl_2IN_2S_2$	63.52	7.54	12.66	2.80	6.40
Ic	14	210–213	545 sh (4.72), 584 (5.34)	65.22	7.93	11.82	2.39	5.80	$C_{59}H_{87}Cl_2IN_2S_2$	65.23	8.07	11.68	2.58	5.90
Id	13	210–213	548 sh (4.71), 585 (5.32)	59.01	6.63	13.48	3.18	6.80	$C_{47}H_{62}Cl_3IN_2S_2$	59.27	6.56	13.33	2.94	6.73
Ie	23	202–205	547 sh (4.71), 585 (5.21)	61.33	7.16	12.57	2.70	6.27	$C_{53}H_{74}Cl_3IN_2S_2$	61.41	7.20	12.24	2.70	6.19
If	28	197–200	548 sh (4.74), 585 (5.36)	63.37	7.57	11.49	2.50	5.67	$C_{59}H_{86}Cl_3IN_2S_2$	63.23	7.73	11.32	2.50	5.72
Ig	11	248–250	547 (4.60), 585 (5.21)	59.87	6.63	13.66	3.16	6.96	$C_{47}H_{62}Cl_2FIN_2S_2$	60.31	6.68	13.56	2.99	6.85
Ih	11	245–247	547 sh (4.71), 585 (5.33)	62.09	7.49	12.40	2.68	6.20	$C_{53}H_{74}Cl_2FIN_2S_2$	62.41	7.31	12.44	2.74	6.27
Ii	14	242–244	546 sh (4.69), 585 (5.32)	64.47	8.02	11.45	2.51	5.70	$C_{59}H_{86}Cl_2FIN_2S_2$	64.18	7.85	11.49	2.53	5.80
IVa	26	112–114		57.14	6.40	–	2.59	11.70	$C_{26}H_{35}Cl_2NS_2O_3$	57.34	6.48	–	2.57	11.78
IVb	39	110–113		59.18	7.09	–	2.34	10.52	$C_{29}H_{41}Cl_2NS_2O_3$	59.37	7.04	–	2.39	10.93
IVc	37	108–110		61.46	7.86	–	2.25	10.20	$C_{32}H_{47}Cl_2NS_2O_3$	61.12	7.54	–	2.23	10.20

Table 3. ^{1}H NMR spectra of compounds **I–IV**

Compd. no.	δ, ppm									
	CH_3	CH_2	NCH_2	*o*-H (2H)	*m*-H (2H)	*p*-H (1H)	H^4	H^6	H^7	$H^α$ (2H)
Ia	0.83 (6H)	1.10–1.40 (32H), 1.61 (4H), 1.90 (4H)	4.59 (4H)	7.37	7.68	7.73	7.17 (2H)	7.13 (2H)	7.19 (2H)	7.95
Ib	0.84 (6H)	1.10–1.45 (44H), 1.57 (4H), 1.90 (4H)	4.59 (4H)	7.37	7.69	7.74	7.17 (2H)	7.14 (2H)	7.20 (2H)	7.96
Ic	0.81 (6H)	1.12–1.37 (56H), 1.56 (4H), 1.86 (4H)	4.56 (4H)	7.31	7.64	7.70	7.16 (2H)	7.10 (2H)	7.16 (2H)	7.90
Id	0.85 (6H)	1.17–1.40 (32H), 1.62 (4H), 1.91 (4H)	4.62 (4H)	7.32	7.68	–	7.20 (2H)	7.17 (2H)	7.27 (2H)	8.04
Ie	0.86 (6H)	1.15–1.40 (44H), 1.61 (4H), 1.90 (4H)	4.62 (4H)	7.32	7.68	–	7.21 (2H)	7.17 (2H)	7.27 (2H)	8.04
If	0.85 (6H)	1.15–1.40 (56H), 1.60 (4H), 1.90 (4H)	4.60 (4H)	7.32	7.68	–	7.20 (2H)	7.17 (2H)	7.26 (2H)	8.01
Ig	0.84 (6H)	1.10–1.47 (32H), 1.61 (4H), 1.89 (4H)	4.60 (4H)	7.35	7.39	–	7.20 (2H)	7.16 (2H)	7.24 (2H)	8.03
Ih	0.86 (6H)	1.20–1.40 (44H), 1.62 (4H), 1.91 (4H)	4.61 (4H)	7.37	7.40	–	7.20 (2H)	7.16 (2H)	7.24 (2H)	8.03
Ii	0.88 (6H)	1.20–1.40 (56H), 1.61 (4H), 1.90 (4H)	4.60 (4H)	7.36	7.40	–	7.20 (2H)	7.16 (2H)	7.24 (2H)	8.01
IVa	0.86 (3H), 3.23 (3H)	1.00–1.60 (16H), 1.80 (2H)	4.64 (2H)	7.15	7.60	–	7.70 (1H)	7.57 (1H)	8.08 (1H)	–
IVb	0.82 (3H), 3.23 (3H)	1.00–1.60 (24H), 1.80 (2H)	4.64 (2H)	7.16	7.60	–	7.75 (1H)	7.56 (1H)	8.13 (1H)	–
IVc	0.85 (3H), 3.24 (3H)	1.00–1.50 (30H), 1.80 (2H)	4.65 (2H)	7.15	7.60	–	7.75 (1H)	7.58 (1H)	8.07 (1H)	–

succession with Et_2O and MeCN. The residue was recrystallized from MeCN. Yields obtained under optimum conditions (at 150°C), melting points, and elemental analyses of benzothiazolium salts **IVa–IVc** are given in Table 2, ^1H NMR spectra in Table 3.

By evaporation in a vacuum of acetonitrile filtrate a substance was separated containing according to the ^1H NMR spectrum predominantly 2-methyl-5-chlorobenzothiazole *p*-chlorobenzenesulfonate **V** with a little of salt **IV** as impurity. ^1H NMR spectrum of compound **V**: 3.11 s (3H, Me), 7.28 d (2H, H_{arom}, *J* 7.5 Hz), 7.50 d.d (1H, H^6, J_1 8, J_2 1 Hz), 7.75 d (2H, H_{arom}, *J* 7.5 Hz), 7.84 d (1H, H^7, *J* 8 Hz), 8.13 d (1H, H^4, *J* 1 Hz), 12.40 br.s (1H, NH).

Preparation of 2-[3-(3-alkyl-5-chloro-2(3*H*)-benzothiazolidene)-2-aryl-1-propenyl]-3-alkyl-5-chlorobenzothiazolium iodides (Ia–Ii). A mixture of 2 mmol of the respective benzothiazolium salt **IVa–IVc**, 6 mmol of trimethyl orthobenzoate, ortho(*p*-chlorobenzoate) or ortho(*p*-fluorobenzoate) **VIIIa–VIIIc**, and 2 ml of pyridine (dried over KOH and distilled) was boiled for 1.5 h. The reaction mixture was cooled, poured into ~20% water solution of KI, and extracted with CH_2Cl_2. The extract was washed with 2% HCl and with water, and dried with $CaCl_2$. The solvent was distilled off in a vacuum. The residue was two-fold subjected to chromatography on a column packed with Al_2O_3, collecting a violet fraction of dye (eluent CH_2Cl_2–MeCN, 4:1). The solution was evaporated, the residue was dissolved in CH_2Cl_2 and precipitated with Et_2O. The relatively less stable dyes **If, Ig** were prepared by boiling for 45 min and were subjected only once to chromatography.

The study was carried out under financial support of the Russian Foundation for Basic Researc (grant 02-03-33336) NOW grant 047.009.019.

REFERENCES

1. Alfimov, M.V. and Khairutdinov, R.F., *Fotokhimiya organizovannykh molekulyarnykh sistem* (Photochemistry of Organized Molecular System), Chernogolovka Akad. Nauk SSSR, 1987, p. 59.
2. Tyutyulkov, N., Fabian, J., Mehlhorn, F., Dietz, F., and Tadjer, A., *Polymethine Dyes Structure and Properties*, Sofia, 1991, p. 107.
3. Markov, R.V., Plekhanov, A.I., Rautian, S.G., Safonov, V.P., Orlova, N.A., Shelkovnikov, V.V., and Volkov, V.V., *Opt. i Spektr*., 1998, vol. 85, p. 643.
4. Orlova, N.A., Kolchina, E.F., Zhuravlev, F.A., Shakirov, M.M., Gerasimova, T.N., and Shelkovnikov, V.V., *Khim. Geterotsikl. Soed.*, 2002, vol. 10, p. 1399.
5. Avdeeva, V.I. and Shapiro, B.I., *Zh. Nauchn. i Prikl. Fotografii*, 1997, vol. 42, p. 27.
6. Shelkovnikov, V.V., Zhuravlev, F.A., Orlova, N.A., Plekhanov, A.I., and Safonov, V.P., *J. Mater. Chem.,* 1995, vol. 5, p. 1331.
7. Sondermann, J., *Lieb. Ann.,* 1971, vol. 749, p. 183.
8. Mezheritskii, V.V., Olekhnovich, E.L., Luk'yanov, S.M., and Dorofeenko, G.N., *Ortoefiry v organicheskom sinteze* (Orthoethers in Organic Chemistry), Rostov: Izd. Rostov. Univ., 1976, p. 16.
9. Hada, H., Hanawa, R., Haraguchi, A., and Yonezawa, Y., *J. Phys. Chem*., 1985, vol. 89, p. 560.
10. Shelkovnikov, V.V., Ivanova, Z.M., Orlova, N.A., Gerasimova, T.N., and Plekhanov, A.I., *Opt. i Spektr.,* 2002, vol. 92, p. 958.
11. Formina, L.V. and Lyubich, M.S., *Tekhnologiya registriruyushchikh sred* (Technology of Registering Media), 1989, p. 46.