Russian Journal of General Chemistry, Vol. 74, No. 2, 2004, pp. 271–275. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 2, 2004, pp. 304–308.

Synthesis of Polymethine Dyes Possessing Nonlinear Optical Properties and Preparation of Photoconducting Systems Based Thereupon

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Received December 27, 2002

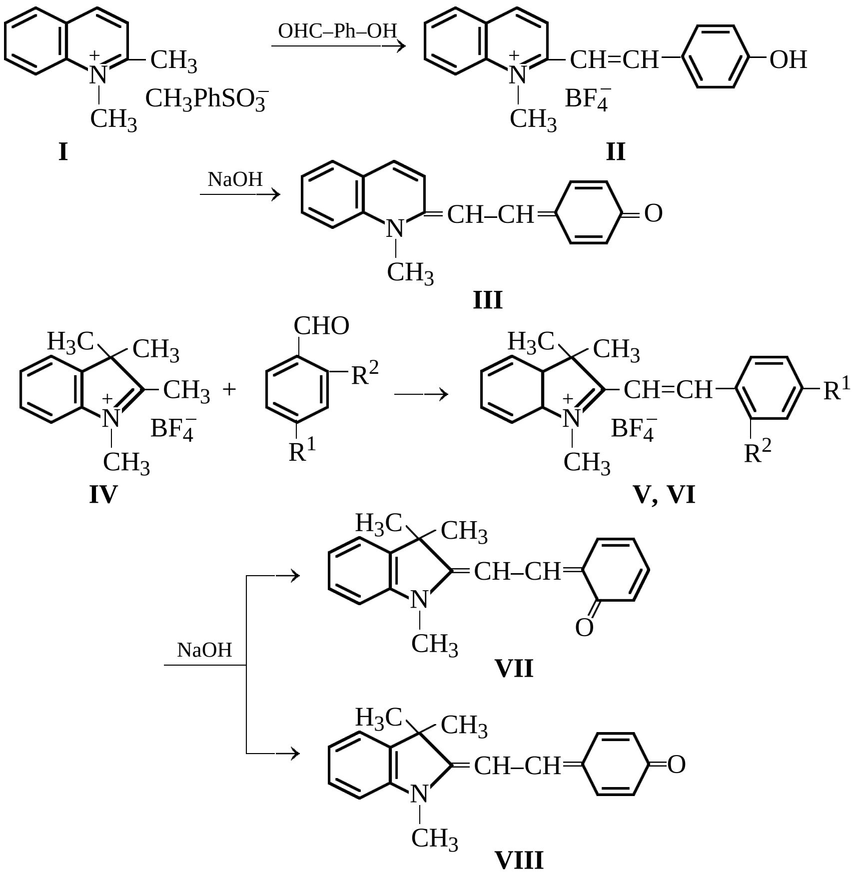
Abstract—Reactions of 2,3,3-trimethyl-3*H*-indolium and 2-methylquinolinium quaternary salts with *o*- and *p*-hydroxybenzaldehydes afforded polymethine dyes (styryls) which were isolated for the first time as the corresponding tetrafluoroborates. The dyes can redily be deprotonated by the action of alkali to obtain neutral merocyanine species. Chemical, photophysical, and optical properties of the products were studied. All the obtained dyes were found to exhibit second-order nonlinear optical activity; in combination with 2,3-dimethylindole, they are also capable of photochemically generating mobile charge carriers.

Organic photorefractive compounds constitute a new promising type of materials for quantum electronics and nonlinear optics. First representatives of such compounds have been reported in early 1990s. Their functioning is based on photorefraction, i.e., modulation of the refractive index of a substance (medium) under irradiation [1]. Polymeric compounds exhibit photorefractive properties when the following conditions are met simultaneously: nonlinear optical activity and photoconductivity [2]. As a rule, this is achieved by introduction into a polymeric matrix of chromophoric units possessing second-order nonlinear optical activity and units capable of effecting photoinduced charge generation and transfer. Just the above approach to design of photorefractive materials is employed in most studies and publications on this topic [3, 4]. According to published data, the most widely used nonlinear optical chromophores are 4-nitrobenzazole derivatives, while photoconducting properties are attached using compositions on the basis of carbazole derivatives [e.g., poly(vinylcarbazole)] [5, 6]. We tried to obtain a chromophore possessing both the properties required. As subjects for study we selected polymethine dyes (cyanines) which are characterized by an extended delocalized π-electron system, high polarizability, and bond leveling [7] and are capable of forming charge-transfer complexes. While our synthetic work being in progress, data in support of our expectations have been published. Hwang *et al.* [8] and Jung *et al.* [9] reported on photorefractive properties of materials containing a single chromophore, namely 6-[3-(6-nitrobenzoxazol-2-yl)-indol-1-yl]-1-hexanol [8] and 1-triphenylamino-2-(*p*-nitrophenyl)ethylene [9].

Our present work reports on the synthesis of polymethine dyes based on 2,3,3-trimethylindolium and 2-methylquinolinium quaternary salts and their chemical, photophysical, and optical properties. Quaternary 2,3,3-trimethylindolium and 2-methylquinolinium salts were prepared by alkylation of the corresponding free bases, 2-methylquinoline and 2,3,3-trimethyl-3*H*-indole, with methyl *p*-toluenesulfonate and methyl benzenesulfonate. 1,2,3,3-Tetramethyl-3*H*-indolium benzenesulfonate was converted into previously unknown tetrafluoroborate **IV**. The use of quaternary salts as one of the components in the synthesis of dyes based on 2-methylquinoline is a common matter, while they are not used typically in the synthesis of dyes on the basis of 1,2,3,3-tetramethylindolium. In the latter case, Fischer’s aldehyde and 2-methylenedihydroindole [10, 11] are generally used instead. We have synthesized dyes **V**–**VIII** by condensation of quaternary salts **I** and **IV** with *o*- and *p*-hydroxybenzaldehydes (Scheme 1).

All the obtained dyes exhibit solvatochromic properties. Table 1 contains their electronic absorption spectra. The dyes with a hydroxy group in the *para* position of the benzene ring (compounds **II** and **VI**) and their merocyanine forms **III** and **VIII** are characterized by distinct splitting of the long-wave absorption band. In the spectrum of **III**, two absorption

Scheme 1.



V, R^1 = H, R^2 = OH; **VI**, R^1 = OH, R^2 = H.

maxima of approximately equal intensities are present. The origin of these maxima is a matter of discussion. Some authors [12] believe that the observed two long-wave maxima belong to two stereoisomers (*cis* and *trans*). According to the other authors [13], the corresponding dimers are formed in solution. However, the formation of dimers seems to be hardly probable, for the spectral pattern does not depend on the dye concentration. On the other hand, the formation of stereoisomers in the transformation of merocyanine structure **III** into dipolar (upon absorption of a quantum of light) is quite possible. Insofar as the band intensities are similar, the formation of both the *cis* and *trans* isomer is equally probable. In the electronic absorption spectrum of cationic dye **II**, one long-wave maximum is more intense; this syggests that one of the isomers prevails. Presumably, the major isomer is *trans*, for *trans* isomers usually absorb at longer wavelengths as compared to the respective *cis* isomers [14].

Table 1. Spectral parameters of 2,3-dimethylindole and compounds **I–IV** and **VI–VIII**

Compound (no.)	Solvent	λ_{max}, nm (log ε)
2,3-Dimethyl-indole	2-Propanol	230 (4.49), 280 (3.87)
I	"	320 (4.95)
II	"	430 (3.9), 582 (4.5)
III	"	437 (4.83), 580 (4.86)
	Chloroform	447 (4.75), 580 (4.79)
IV	2-Propanol	280 (5.1)
VI	"	515 (3.52), 548 (3.88)
VII	"	455 (3.14)
VIII	"	515 (4.69), 547 (5.05)
	Chloroform	510 (4.57), 544 (4.98)

Both cationic dye **II** and its merocyanine form **III** show luminescence properties independendly at each of the absorption maxima. The absorption maxima at λ 447 and 580 nm in the spectrum of **III** correspond to the luminescence maxima at λ 532 and 630 nm, respectively, while the absorption maxima at λ 420 and 570 nm in the spectrum of **II** correspond to the luminescence maxima at λ 484 and 622 nm. The luminescence efficiency is low. The luminescence quantum yields reduced to the corresponding absorption intensity are 5.3×10^{-3} and 6.4×10^{-3} (**III**) and 2.1×10^{-2} and 1.0×10^{-3} (**II**). Independent luminescence at each absorption maximum of dyes **II** and **III** provides an additional support for the existence of stereoisomeric structures.

All the prepared dyes in crystal possess second-order nonlinear optical activity with the following coefficients ($\chi^{(2)} \times 10^{-9}$, SGSE): 0.22 (**II**), 2.40 (**III**), 0.98 (**VI**), 0.16 (**VII**), 1.50 (**VIII**). It is seen that the activity of merocyanine dyes is higher by an order of magnitude and is comparable with the efficiecy of second harmonic generation of urea ($\chi^{(2)} = 3.40 \times 10^{9}$) [15].

It is known that a chromophoric group responsible for photoconductivity of a polymer should be capable of effectively generating mobile charge carriers upon absorption of a quantum of light [16]. Such an ability is typical of charge-transfer complexes which are formed between π-electron-rich and π-electron-deficient systems [17]. Using quaternary salts **I** and **IV** and dyes derived therefrom as electron-acceptor components and 2,3-dimethylindole as donor, we obtained molecular charge-transfer complexes which gave rise to electronic absorption bands in the visible region (no such absorption was observed in the spectra of the initial compounds). The ability of these complexes to generate mobile charge carriers was estimated by studying electrophotographic sensitivity of polymeric films [on the basis of poly(butyl methacrylate)] containing the complexes. Table 2 contains absorption maxima of the charge-transfer complexes and light sensitivities of an $S_{0.1}$ of polymeric layers at the absorption maximum, which were determined from the decrease in the surface potential (by 10%) on exposure to white light. The quantum yield η of photogeneration of charge carrier for all the examined charge-transfer complexes was 0.1–0.2. The rate of surface potential drop in the dark ranges from 1 to 3%/s, indicating good dielectric properties of the polymeric layers. It should be noted that the light sensitivity of polymeric films containing the most popular donor–acceptor complexes based on carbazole derivatives of fluorenone (e.g., trinitrofluorenone) is about 10^5–10^6 cm^2/J, while the maximal experimental value of η is 0.4 [18–20].

Thus, the synthesized polymethine dyes exhibit second-order nonlinear optical properties and are capable of generating mobile charge carriers on exposure to light, which makes them promising as chromophoric species for photorefractive materials.

Table 2. Light sensitivity at the absorption maximum of polymeric films containing charge-transfer complexes

Molecular complex	λ_{max}, nm (log ε) (2-propanol)	$S_{0.1} \times 10^5$, cm^2/J
1,2,3,3-Tetramethyl-3*H*-indolium tetrafluoroborate–2,3-dimethylindole	550 (2.94)	~1
1,2-Dimethylquinolinium *p*-toluenesulfonate–2,3-dimethylindole	500 (3.32)	0.5
1-Methyl-2-(4-hydroxystyryl)-quinolinium tetrafluoroborate–2,3-dimethylindole	563 (2.13)	1.2

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer (200.1 MHz); the chemical shifts were measured relative to signals from residual protons in the solvent. The electronic absorption spectra were determined on a Specord M-400 spectrophotometer. The luminescence spectra were measured using a setup described in [21]. Second harmonic generation was effected using an YAG-Nd^3+ pulse laser operating in the modulated quality factor mode (wavelength 1.06 μm, pulse width 10 ns). The pulse energy was varied over a wide range (up to 30 mJ). The laser beam was adjusted to a Gauss profile via selection of transversal modes with the aid of a diaphragm built into the resonator. A part of the irradiation energy (4%) was split with a beam splitter and was passed to an FD-24K photodiode to monitor the exciting radiation energy. The main part of *p*-polarized radiation was focused onto a sample with a lense (F = 100 mm). The second-harmonic radiation was directed to an MDR-2 gitter monochromator and then to an FEU-106 multiplier. Electric signals from the two photoreceivers were sent to integrating AD transducers and (via CAMAC interface) to a PC for further processing.

Photoinduced surface potential drop was measured as follows. Polymeric films were prepared from solutions of poly(butyl methacrylate) ($M = 2.5 \times 10^6$) and charge-transfer complexes in cyclohexanone, which were applied to glass plates coated with a transparent conductor layer (ITO In_2O_3/SnO_2). The concentration of the complexes was about 15 wt %. The glass plate-supported films were dried for 24 h at 50°C and kept for 12 h at 90°C. The light sensitivity and quantum yields for generation of charge carriers were measured in the electrophotographic mode according to the procedures described in [19, 20] at the Vavilov State Optical Institute (St. Petersburg, Russia).

2,3-Dimethylindole was prepared by the procedure reported in [22]. Yield 91%, mp 109°C [23].

1,2-Dimethylquinolinium *p*-toluenesulfonate (I) was prepared by fusion of equimolar amounts of 2-methylquinoline and methyl *p*-toluenesulfonate at 120°C (reaction time 5 min). Yield 81%, mp 56°C.

1,2,3,3-Tetramethyl-3*H*-indolium tetrafluoroborate (IV). A mixture of 10.0 g of 2,3-dimethylindole and 14.7 g of methyl benzenesulfonate was heated for 4 h at 170°C. The mixture was dissolved in water, the solution was treated with charcoal on heating to the boiling point and filtered, and anhydrous sodium tetrafluoroborate was added to the warm filtrate. The precipitate was filtered off and purified by reprecipitation from ethanol with diethyl ether. Yield 8.6 g (71%), mp 198.5°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.5 s [6H, $C(CH_3)_2$], 2.8 s (3H, CCH_3), 4.0 s (3H, NCH_3), 7.6 s (2H, H_{arom}), 7.8 d (2H, H_{arom}).

Compounds **II**, **V**, and **VI** were synthesized following the general procedure described in [24].

2-(4-Hydroxystyryl)-1-methylquinolinium tetrafluoroborate (II). A mixture of equimolar amounts (4.08 mmol) of compound **I** (1.0 g), *p*-hydroxybenzaldehyde (0.49 g), and piperidine (0.35 g) in 5.5 ml of ethanol was heated for 80 min under reflux. Dye **II** (tetrafluoroborate) was isolated by adding anhydrous sodium tetrafluoroborate to a solution of the reaction mixture in water. Yield 1.06 g (67%), mp 181°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.9 s (3H, NCH_3), 6.2 d (2H, H_{arom}), 6.35 s (1H, OH), 6.58 d (1H), 7.32 t (1H), 7.5 d (2H, H_{arom}), 7.6–7.95 (6H, quinoline ring).

2-(2-Hydroxystyryl)-1,3,3-trimethyl-3*H*-indolium tetrafluoroborate (V) was synthesized in a similar way. The resulting salt was converted into the corresponding merocyanine form.

2-(4-Hydroxystyryl)-1,3,3-trimethyl-3*H*-indolium tetrafluoroborate (VI). Yield 88%, mp 169.5°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.5 s (6H, CCH_3); 4.0 s (3H, NCH_3); 6.6 d (1H), 7.0 t (1H), 6.2 d (2H), and 7.5 d (2H) (H_{arom}), 7.5–8.2 m (4H).

Merocyanine dyes **III**, **VII**, and **VIII** were synthesized according to the procedure described in [25].

4-[2-(1-Methyl-1,2-dihydroquinolin-2-ylidene)-ethylidene]-2,5-cyclohexadienone (III). A mixture of equimolar amounts (2 mmol) of compound **I**, *p*-hydroxybenzaldehyde, and piperidine in 5 ml of ethanol was heated for 2.5 h under reflux. The precipitate was filtered off and dispersed in 100 ml of a 0.2 M solution of KOH, the suspension was stirred at 70–72°C until the dye dissolved, and the precipitate was filtered off and washed with water until neutral washings. Yield 0.82 g (85%), mp 205°C; published data [26]: mp 208°C.

6-[2-(1,3,3-Trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)ethylidene]-2,4-cyclohexadienone (VII). Yield 83%, mp 163°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.2 d [6H, $C(CH_3)_2$], 4.1 s (3H, NCH_3), 5.7 d (1H, =CH), 6.6 d (1H, CH=), 6.8 m (2H, quinone ring), 6.9–7.3 m (4H, indole), 7.6 m (2H, quinone ring).

4-[2-(1,3,3-Trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)ethylidene]-2,5-cyclohexadienone (VIII). Yield 89%, mp 62°C [27].

ACKNOWLEDGMENTS

The authors are grateful to E.L. Aleksandrov (Vavilov State Optical Institute, St. Petersburg, Russia) for measuring the electrophotographic sensitivities of polymeric films and N.I. Rtishchev (St. Petersburg State Institute of Technology, St. Petersburg, Russia) for studying luminescence properties of the dyes.

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