Synthesis of pseudocyanines containing unsaturated groups at the nitrogen atom

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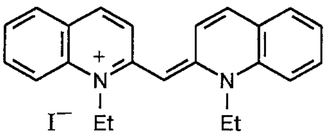
A new method for synthesis of 1-[(2-acryloyloxyethyl)- and 1-[(2-propenyl)-2-(2-(1*H*)-quinolidene)-methyl]-1-ethylquinolinium iodides was proposed. The structures of the dyes obtained were studied by ^{1}H NMR spectroscopy.

Key words: pseudocyanines, *N*-acryloyloxyethyl and *N*-alkyl derivatives, quinolinium salts, synthesis.

Within the last decade an important role for organized molecular structures has been discovered in the creation of new optical systems for information recording and processing. *J*-aggregates of cyanine dyes are of great interest because their use makes it possible to perform spectral data compression.[1,2]

Previously[3] we developed a procedure for the preparation of *J*-aggregates of pseudocyanine (**1**) in polyvinylpyrrolidone films and showed a possibility of selective disaggregation under the action of laser irradiation[3] and a high level of cubic optical nonlinearity of the film structures produced.[4]

Examples are known of producing aggregated structures of dyes with optical and nonlinear optical properties, differing from those of a monomeric form, by covalent[5] or ionic[6] binding of the chromophore with polymer. In relation to this we synthesized dyes of type **1**, containing an acryloyl or vinyl substituted alkyl group at the nitrogen atom, in order to create polymeric *J*-aggregates based on them.



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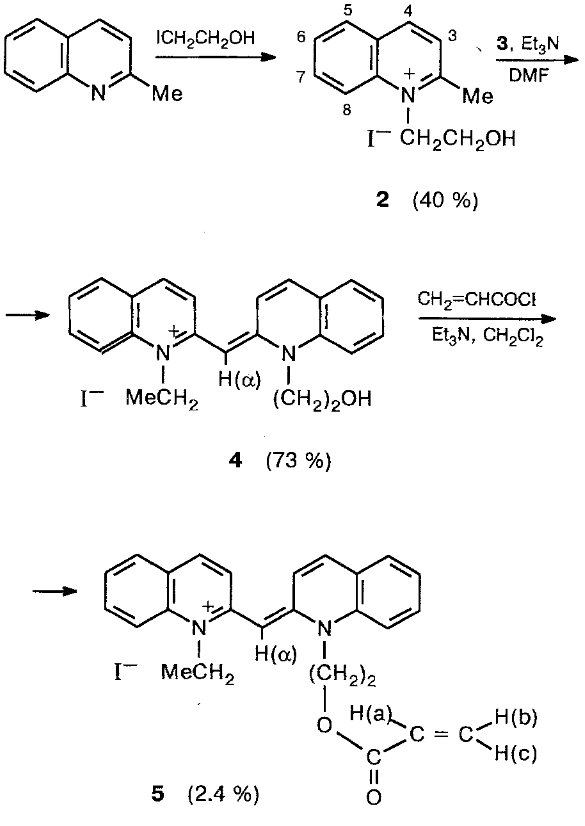
Condensation of 2-methylquinolinium salts with 2-iodo- or 2-(alkylthio) quinolinium salts[7] is the most commonly used technique for synthesis of pseudocyanines. We considered condensation with quinolinium salts containing an acryloyl substituent to be improbable because of the extremely high polymerizability of the latter. For this reason, we synthesized pseudocyanine with a β-oxyethyl group at the 1-position, followed by its acylation.

The starting compound 1-(2-hydroxyethyl)-2-methylquinolinium iodide (**2**) was prepared by boiling quinaldine with 2-iodoethanol. The structure of **2** is confirmed by its ^{1}H NMR spectrum and elemental analysis data. The quaternary salt of **2** was introduced in the reaction with 1-ethyl-2-(ethylthio)quinolinium iodide (**3**) obtained by



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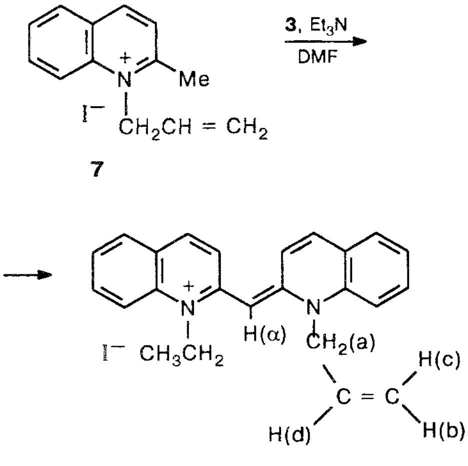
the procedure reported earlier.[7] Heating in DMF in the presence of triethylamine resulted in dye (**4**) in a good yield, whose structure was supported by elemental analysis data, ^{1}H NMR spectrum, and electronic absorption spectrum (EA), which is similar to that of pseudocyanine **1**. An attempt to perform the condensation by heating the reagents in pyridine led to the isolation of mainly the starting compounds.

The acylation of dye **4** with acryloyl chloride in dichloromethane in the presence of triethylamine gives a complex mixture of products even under mild conditions (at 0 °C) from which pseudocyanine (**5**) was isolated by preparative TLC. Like dye **1**, compound **5** shows absorption bands in the region of 500—530 nm of the electronic absorption spectrum. The ^{1}H NMR spectrum includes signals of a $COCH{=}CH_2$ group, supporting the presence of an acryloyl moiety in molecule **5**. We believe that the small yield of dye **5** results from its high polymerizability. In accordance with this, pseudocyanine (**6**), containing the less reactive allyl group in position 1, was easily synthesized by heating the quaternary salt (**7**) reported earlier[8] with 2-(ethylthio)quinoline iodoethylate **3** in DMF in the presence of triethylamine.

The results of creating the polymeric structures based on dyes **5** and **6** and their spectral studies will be published in further papers.



7

6 (31 %)

Experimental

^{1}H NMR spectra were obtained on Bruker WP-200SY and Bruker AC-200 spectrometers (200 MHz). Electronic absorption spectra were recorded on a Specord M-40 instrument; the long-wave spectral region is given.

1-(2-Hydroxyethyl)-2-methylquinolinium iodide (2).* A mixture of quinaldine (2.12 g, 14 mmol) and ethylene iodohydrin (4.8 g, 28 mmol) was heated at 100—110 °C for 4 h in an oil bath; after cooling ether was added, and the precipitate formed was filtered off and washed with ether (containing added ethanol) to give salt **2** (1.84 g, 40 %, m.p. 209—212 °C (from ethanol). Found (%): C, 45.71; H, 4.43; I, 39.90; N, 4.43. $(C_{12}H_{14}NO)^+I^-$. Calculated (%): C, 45.73; H, 4.48; I, 40.27; N, 4.44. ^{1}H NMR spectrum (DMSO), δ: 3.18 (s, 3 H, CH_3); 4.0 (t, 2 H, $CH_2C\underline{H}_2OH$, J = 5.5 Hz); 5.18 (t, 2 H, $C\underline{H}_2CH_2OH$, J = 5.5 Hz); 7.97 (t, 1 H, H(6), J = 7.5 Hz); 8.08—8.23 (m, 2 H, H(3), H(7)); 8.43 (d, 1 H, H(5), J = 7.5 Hz); 8.62 (d, 1 H, H(8), J = 8.5 Hz); 9.13 (d, 1 H, H(4), J = 8.5 Hz).

2-[1-(2-Hydroxyethyl)-(2-(1*H*)-quinolinylidene)methyl]-1-ethylquinolinium iodide (4). Triethylamine (2 mL) was added to a solution of salt **2** (0.83 g, 2.6 mmol) and 1-ethyl-2-(ethylthio)quinolinium iodide **3** (0.9 g, 2.6 mmol), synthesized by the reported procedure,[7] in dry DMFA (10 mL); and the reaction mixture was heated at 100—105 °C for 2 h with stirring and cooled. The precipitate formed was filtered off, thoroughly washed with ether to give dye **4** (0.9 g, 73 %), m.p. 262—265 °C (decomp.) (from ethanol). Found (%): C, 58.49; H, 4.82; I, 27.17. $(C_{23}H_{23}N_2O)^+I^-$. Calculated (%): C, 58.73; H, 4.93; I, 26.98. EA (EtOH), λ_{max}/nm: 498 (ε 40300), 532 (ε 59700). ^{1}H NMR spectrum (DMSO), δ: 1.50 (t, 3 H, $C\underline{H}_3CH_2$, J = 7 Hz); 4.10 (q, 2 H, $CH_2C\underline{H}_2OH$, J = 5 Hz); 4.51 (q, 2 H, $CH_3C\underline{H}_2$, J = 7 Hz); 4.70 (t, 2 H, $C\underline{H}_2CH_2OH$, J = 5 Hz); 5.43 (t, 1 H, OH, J = 5 Hz); 6.31 (s, 1 H, H(α)); 7.52 (td, 2 H, H(7), H(7') or H(6), H(6'), J_1 = 7.5 Hz, J_2 = 3 Hz); 7.75—8.00 (m, 8H arom); 8.13 (dd, 2 H, H(6), H(6') or H(7), H(7'), J_1 = 8.5 Hz, J_2 = 7.5 Hz).

2-[1-(2-Acryloyloxyethyl)-(2-(1*H*)-quinolinylidene)-methyl]-1-ethylquinolinium iodide (5). A solution of acryloyl chloride (1 mL, 15 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a mixture of dye **4** (0.64 g, 1.5 mmol), triethylamine (1 mL), and hydroquinone (0.05 g) in 5 mL of dry CH_2Cl_2 with stirring and cooling in an ice bath. The reaction mixture was stirred for 20 min, poured into water, and extracted with CH_2Cl_2.* The extract was washed with water, dried over $CaCl_2$, and evaporated to produce an oily dark cherry product (0.14 g), from which dye **5**** (0.017 g, 2.4 %) was isolated by preparative TLC on Al_2O_3 plates [eluent — a 1:1 (vol) mixture of CH_3CN and CH_2Cl_2], decomp. p. ~130 °C (reprecipitation from MeCN in ether). Found (%): C, 59.63; H, 4.88; I, 24.17; N, 5.11. $(C_{26}H_{25}N_2O_2)^+I^-$. Calculated (%): C, 59.55; H, 4.81; I, 24.20; N, 5.34. EA (CH_2Cl_2), λ_{max}/nm: 502 (ε 46100), 534 (ε 68300). ^{1}H NMR (CD_2Cl_2) δ: 1.49 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.5 Hz); 4.47 (q, 2 H, $CH_3C\underline{H}_2$, J = 7.5 Hz); 4.52—4.73 (m, 4 H, $(CH_2)_2$); 5.71 (dd, 1 H, H(b), J_1 = 10 Hz, J_2 = 1.5 Hz); 5.72 (s, 1 H, H(α)); 5.93 (dd, 1 H, H(a), J_1 = 17 Hz, J_2 = 10 Hz); 6.23 (dd, 1 H, H(c), J_1 = 17 Hz, J_2 = 1.5 Hz); 7.27—7.94 (m, 12 H arom).

2-[1-(2-Propenyl)-(2-(1*H*)-quinolinylidene)methyl]-1-ethylquinolinium iodide (6). A mixture of 2-methyl-1-(2-propenylquinolinium iodide **7***** (0.31 g, 1 mmol) (obtained by refluxing quinaldine with twofold mole excess of allyl iodide), salt **3** (0.35 g, 1 mmol), and triethylamine (1 mL) in

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* Compound **2** was used in the synthesis of heterocyclic azomethines;[9] no information is available concerning its synthesis and specific features.

* A portion of the precipitate between phases was not dissolved.

** A wide colored band remains at the take-off position, which can not be eluted with any eluents.

*** M.p. and ^{1}H NMR data are identical to those for the compound reported earlier.[10]

3 mL of DMFA was heated at a bath temperature 100 °C for 1.5 h with stirring and cooled. After cooling the precipitate formed was filtered off, washed with ether, and dried in air to give dye **6** (0.21 g, 31 %), m.p. 232—235 °C (reprecipitation from MeCN in ether). Found (%): C, 61.71; H, 4.91; I, 27.20; N, 6.03. $(C_{24}H_{23}N_2)^{+}I^{-}$. Calculated (%): C, 61.81; H, 4.97; I, 27.21; N, 6.01. EA (CH_2Cl_2), λ_{max}/nm: 508 (ε 43500), 529 (ε 88500). ^1H NMR ($CDCl_3$), δ: 1.52 (t, 3 H, $\underline{CH_3}CH_2$, J = 7 Hz); 4.46 (q, 2 H, $CH_3\underline{CH_2}$, J = 7 Hz); 5.00 (d, 1 H, H(c), J = 17 Hz); 5.09 (br. s., 2 H, H(a)); 5.40 (d, 1 H, H(b), J = 10 Hz); 5.48 (s, 1 H, H(α)); 6.24 (m, 1 H, H(d)); 7.28—7.87 (m, 10 H arom); 8.06 (t, 2 H, H(6), H(6') or H(7), H(7'), J = 9 Hz).

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References

1. N. Tyutyulkov, J. Fabian, A. Mehlhorn, F. Dietz, and A. Tadjer, *Polymethine Dyes. Structure and Properties*, Sofia, 1991, 107.
2. C. Ishimoto, H. Tomimuro, and J. Seto, *Appl. Phys. Lett.*, 1986, **49**, 1677.
3. A. L. Grebelkin, I. K. Korobeinicheva, N. A. Orlova, S. M. Repinskii, L. L. Sveshnikova, Zh. Yu. Selyunina, N. I. Sagalaeva, and V. V. Shelkovnikov, *Zh. Nauchn. Prikl. Fotograf.* [*J. Scient. Appl. Photogr.*], 1992, **37**, 232 (in Russian).
4. F. A. Zhuravlev, N. A. Orlova, V. V. Shelkovnikov, A. I. Plekhanov, S. G. Rautian, and V. P. Safonov, *JETP Lett.*, 1992, **56**, 260.
5. G. J. Smats and B. Simionescu, *Makromol. Chem.*, 1977, **178**, 2719.
6. S. Namura, T. Kobayashi, H. Matsuda, S. Okada, H. Nakanishi, and H. Tomiyama, *Chem. Phys. Lett.*, 1990, **175**, 398.
7. B. Beilenson and F. M. Hamer, *J. Chem. Soc.*, 1939, 143.
8. E. Macovski and E. Ramontiani, *J. Pract. Chem.*, 1932, **135**, 137.
9. W. Schulze, W. Jungstand, W. Gutsche, K. Wohlrabe, K. Kramarczyk, and D. Tresselt, *Pharmazie*, 1977, **32**, 271.
10. R. K. Hill and G. R. Newkome, *Tetrahedron Lett.*, 1968, 5059.

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