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ScienceDirect
Dyes and Pigments 73 (2007) 344–352
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis and properties of barbiturate indolenine heptamethinecyanine dyes

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Received 7 December 2005; accepted 9 January 2006
Available online 4 April 2006

Abstract

Indolenine and benzindolenine heptamethinecyanine dyes having barbiturate at meso position were synthesized by the substitution of corresponding meso chloro substituted dyes with barbituric acid, and their absorption spectra and crystal structures were investigated. All barbiturate dyes had absorption near 800 nm and showed hypsochromic shift from the corresponding chloro dyes. Both barbiturate and chloro benzindolenine dyes showed bathochromic shift from the corresponding indolenine dyes. The crystal structures of barbiturate dyes indicated that barbiturate ring is sterically hindered by indolenine ring and cannot form adequate π-conjugation with cyanine main chromophore.

Keywords: Cyanine; Heptamethine; Indolenine; Barbiturate; Absorption spectra; Crystal structure

1. Introduction

Cyanine dyes are researched widely as functional dyes [1–4]. Especially, indolenine cyanine dyes are expected from their superior solubility and their strong absorption in near infrared region, as to the sensitized material for near infrared laser such as GaAs semiconductor. An introduction of an electron-donating substituent at meso position in a trimethine cyanine system contributes to light-fastness of dyes [5]. For long poly methine chains, replacement of an ethylene unit by a cyclic conjugated bridge is well known to improve the stability of the dye. Concerning the absorption shift of cyanine dyes, some rules are known [6]. Then, barbituric acid has been used as disperse dyes with strong fluorescent and as yellow organic pigments [7]. In this paper, the indolenine heptamethinecyanine dyes (**4a, b, 4′a, b, 4″a,b**) having barbiturate substitute at the meso position of the molecule and having absorption bands near 780and 830 nm were synthesized (Scheme 1), and their absorption spectra and crystal structures were investigated.

2. Experimental

2.1. General

IR spectra were recorded on a JASCO FTIR-410 using potassium bromide pellet. ^{1}H NMR spectra were recorded on JEOL JNM ECP-500 and JNM AL-300 in DMSO-d_6. FAB mass spectra were recorded on JEOL MS-700. Vis–NIR spectra were recorded using HITATI 330 and JASCO V-570.

2.2. Preparation of anilinium salts and indolenium salts

Anilinium salts **1**, **1′**, **1″** and indolenium salts **2a**, **2b** were prepared by known similar method [8–10]. Anilinium salts **1**, **1′**, **1″** having 6, 5 and 7 member ring structure methine chain, and benzindolenium and indolenium salts **2a**, **b** were synthesized from cyclohexanone, cyclopentanone, cyclohepatanone, benzindolenine and indolenine, respectively.

2.2.1. *N-[5-Anilino-3-chloro-2,4-(propane-1,3-diyl)-2,4-pentadiene-1-ylidene]anilinium chloride (anilinium salt (**1**))*

Under nitrogen atmosphere, to DMF (13 ml, 0.17 mol) was added dropwise phosphoryl chloride (11 ml, 0.12 mol) slowly

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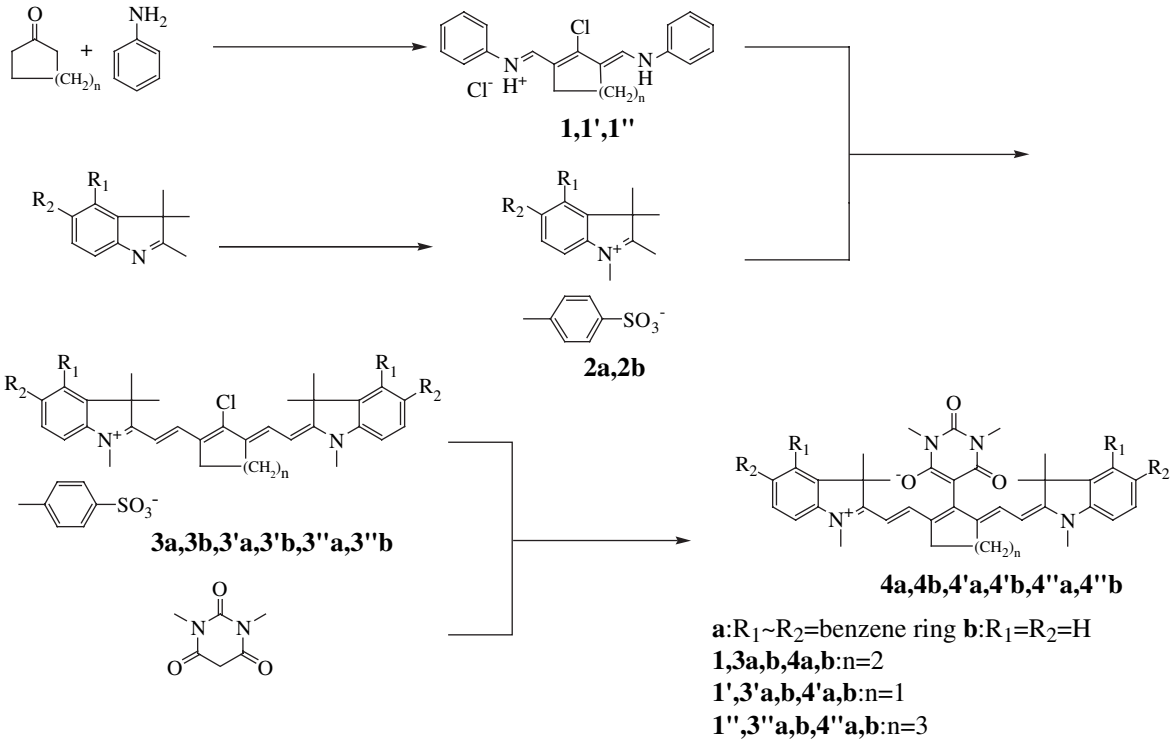
0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.01.039



Scheme 1.

at 0 °C and the solution was stirred for 30 min. Cyclohexanone (5.5 ml, 0.053 mol), was added and the mixture was refluxed for 1 h. The solution was cooled to 20 °C, 18 mlaniline/EtOH [1:1 (v/v)] was added dropwise gradually to the solution, and stirred for 30 min. The mixture was poured into chilled 110 ml water/conc. HCl (10:1) and cooled for 2 h in an ice cold bath. The solid was filtered and washed with cold water, Et_2O and acetone. **1** was obtained as a purple powder (8.67 g, 45.6%) (87% [8]).

^{1}H NMR (300 MHz, DMSO-*d*): 8.54 (s, 2H, −CH═), 7.64 (d, $J = 7.8$ Hz, 4H, Ar−H), 7.47 (t, $J = 7.8$ Hz, 4H, Ar−H), 7.27 (m, 4H, Ar−H), 2.75 (t, $J = 6.0$ Hz, 4H, $-CH_2-$), 1.85 (m, 2H, $-CH_2-$); FAB-MS (*m/z*): 323 [M − Cl$^-$]; λ_{max}/nm [ε]: 517 [2.76×10^5]; mp (°C): 194 (220[8]).

2.2.2. *N-[5-Anilino-3-chloro-2,4-(ethane-1,3-diyl)-2,4-pentadiene-1-ylidene]anilinium chloride (anilinium salt (**1′**))*

To a solution of *N*-methylformanilide (13.5 g) in chloroform (12.5 ml) was added oxy phosphorus chloride (14 ml) at 10 °C. After 1 h stirring at room temperature, the solution was added to cyclopentanone (3.36 g, 0.030 mol) and stirred for 4 h at 50 °C. After cooling to room temperature, to the mixture was added potassium carbonate (10 g), then added aniline (8.4 g), conc. hydrochloric acid (7.5 ml) and water (50 ml), and the mixture was stirred for 1 h at room temperature. Next, to the mixture was added dichloromethane (50 ml) and allowed to stand for a while. The precipitated solid was filtered and washed with acetone and water to obtain anilinium salt **1′** (8.69 g, 84.1%).

^{1}H NMR (300 MHz, DMSO-*d*): 8.31 (s, 2H, −CH═), 7.59−7.57 (d, $J = 7.5$ Hz, 4H, Ar−H), 7.47−7.43 (t, $J = 7.8$ Hz, 4H, Ar−H), 7.27−7.23 (t, $J = 6.9$ Hz, 2H, Ar−H), 2.99 (s, 4H, $-CH_2-$); FAB-MS (*m/z*): 309 [M − Cl$^-$]; λ_{max}/nm [ε]: 529 [4.19×10^4]; mp (°C): 197−200.

2.2.3. *N-[5-Anilino-3-chloro-2,4-(butane-1,3-diyl)-2,4-pentadiene-1-ylidene]anilinium chloride (anilinium salt (**1″**))*

To a solution of *N*-methylformanilide (13.5 g) in chloroform (12.5 ml) was added oxy phosphorus chloride (14 ml) at 10 °C. After 1 h stirring at room temperature, to the solution was added cycloheptanone (2.52 g, 0.030 mol) and the mixture was stirred for 4 h at 50 °C. After cooling to room temperature, to the mixture was added potassium carbonate (10 g), then was added aniline (8.4 g), conc. hydrochloric acid (7.5 ml) and water (50 ml), and the mixture was stirred for 1 h at room temperature. Next, dichloromethane (50 ml) was added to the mixture and the mixture was stirred for 1 h at room temperature. After standing for a while, precipitated solid was filtered and washed with acetone and water to obtain anilinium salt **1″** (4.89 g, 43.7%) (48.9% [9]).

^{1}H NMR (500 MHz, DMSO-*d*): 8.56 (s, 2H, −CH═), 7.57−7.55 (d, $J = 8.0$ Hz, 4H, Ar−H),7.48−7.45 (t, $J = 7.3$ Hz, 4H, Ar−H), 7.29−7.26 (t, $J = 7.3$ Hz, 2H, Ar−H),2.78 (s, 4H, $-CH_2-$), 1.82 (m, 2H, $-CH_2-$); FAB-MS (*m/z*): 338 [M − Cl$^-$]; λ_{max}/nm [ε]: 520[4.19×10^4]; mp(°): 157−160.

2.2.4. *1H-Benzindolium (1,1,2,3-tetramethyl) salt with 4-methylbenzenesulfonic acid (indolenium salt (**2a**))*

Under nitrogen atmosphere, a solution of large excess methyl *p*-toluene sulfonate (25 g, 0.134 mol) and benzindolenine (10 g, 0.0446 mol) was stirred for 12 h at 140 °C. The precipitated crystal was filtered and washed with acetone to obtain **2a** (14.2 g, 80.0%).

^{1}H NMR (300 MHz, DMSO-*d*): 8.05 (t, $J = 8.4$ Hz, 2H, Ar–H), 7.79–7.26 (m, 4H, Ar–H), 6.90 (d, $J = 7.2$ Hz, 4H, Ar–H), 4.28 (s, 3H, $-CH_3$), 3.06 (s, 3H, $-CH_3$), 2.21 (s, 3H, $-CH_3$), 1.78 (s, 6H, $-CH_3$); FAB-MS (*m/z*): 224 [M − Ts$^-$]; mp(°C): 104.

*2.2.5. 3H-Indolium (1,2,3,3-tetramethyl) salt with 4-methylbenzenesulfonic acid (indolenium salt (**2b**))*

Under nitrogen atmosphere, a solution of the large excessive methyl *p*-toluene sulfonate (25 g, 0.134 mol) and indolenine (12 g) was stirred for 12 h at 140 °C. Red purple oil of **2b** was obtained as a mixed liquid including *p*-toluene sulfonic acid. The mixed liquid was utilized in the synthesis of the next cyanine pigment.

2.3. Preparation of chloro indolenine cyanine dyes

Chloro indolenine cyanine dye **3b** was commercially obtained. Chloro indolenine cyanine dyes **3a**, **3′a**,**b**, and **3″a**,**b** were synthesized from anilinium salts **1** and indolenium salts **2** (mol ratio of **1**:**2** = 1:2) by the similar literature method [1,8–10].

*2.3.1. 1H-Benz[e]indolium,2 ([2-[2-chloro-3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylindene)ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,1,3-trimethyl) salt with 4-methylbenzenesulfonic acid (chloro indolenine cyanine dye (**3a**))*

A solution of indolenium salt **2a** (6 mmol, 2.37 g), anilinium salt **1** (3 mmol, 1.179 g), and sodium acetate (7 mmol, 600 mg) in ethanol (60 ml) was stirred for 1 h at 80 °C under a nitrogen atmosphere. After removing the solvent, the product was purified by silica gel column chromatography (eluent solvent; chloroform: methanol = 19:1) to obtain the cyanine dye **3a** (0.600 g, 81.6%).

^{1}H NMR (300 MHz, DMSO-*d*): 7.47–8.39 (m, 16H), 7.11 (d, $J = 7.8$ Hz, 2H, Ar–H), 6.35 (d, $J = 14.4$ Hz, 2H, –CH=), 3.82 (s, 6H, $-CH_3$), 2.76 (m, 4H, $-CH_2-$), 2.28 (s, 3H, $-CH_3$), 1.96 (s, 12H, $-CH_3$), 1.91 (m, 2H, $-CH_2-$); FAB-MS (*m/z*): 584 [M − Ts$^-$]; λ_{max}/nm [ε]: 826 [3.23×10^5].

*2.3.2. 1H-Benz[e]indolium (2-[2-[2-chloro-3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene)ethylidene]-1-cyclopenten-1-yl]ethenyl]-1,1,3-trimethyl) salt with 4-methylbenzenesulfonic acid (chloro indolenine cyanine dye (**3′a**))*

A solution of anilinium salt **1′** (0.43 g, 1.25 mmol), indolenium salt **2a** (1.085 g, 2.75 mmol), 2-propanol (5 ml), acetic anhydride (0.35 ml) and triethylamine (1.05 ml) was stirred at 50 °C for 1 h, and water (20 ml) was added to the mixture. After filtering, the precipitated product was dissolved in methanol and allowed to stand for a while. To the solution 70 wt % *p*-toluene sulfonic acid hydrate (1.2 ml) was added. After removing the solvent, cyanine dye **3′a** (0.649 g,70.3%) was obtained by the recrystallization of the residue from water and acetone.

^{1}H NMR (500 MHz, DMSO-*d*): 8.26 (d, $J = 9.0$ Hz, 2H, Ar–H), 8.07 (d, $J = 9.0$ Hz, 2H, Ar–H), 8.05 (d, $J = 9.0$ Hz, 2H, Ar–H), 7.84 (d, $J = 14.5$ Hz, 2H, –CH=), 7.75 (d, $J = 9.5$ Hz, 2H, Ar–H), 7.62 (t, $J = 9.0$ Hz, 2H, Ar–H), 7.51 (t, $J = 9.0$ Hz, 2H, Ar–H), 7.45 (d, $J = 9.5$ Hz, 2H, Ar–H), 7.06 (d, $J = 9.5$ Hz, 2H, Ar–H), 6.15 (d, $J = 14.5$ Hz, 2H, –CH=), 3.78 (s, 6H, $-CH_3$), 2.98 (m, 4H, $-CH_2-$), 2.27 (s, 3H, $-CH_3$), 1.93 (s, 12H, $-CH_3$); FAB-MS (*m/z*): 570 [M − Ts$^-$]; λ_{max}/nm [ε]: 850 [3.56×10^5].

*2.3.3. 3H-Indolium (2-[2-[2-chloro-3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene]-1-cyclopenten-1-yl]ethenyl]-1,3,3-trimethyl) salt with 4-methylbenzenesulfonic acid (chloro indolenine cyanine dye (**3′b**))*

A solution of anilinium salt **1′** (0.43 g, 1.25 mmol), indolenium salt **2b** (0.951 g, 2.75 mmol), 2-propanol (5 ml), acetic anhydride (0.35 ml) and triethylamine (1.05 ml) was stirred at 50 °C for 1 h and to the mixture water (20 ml) was added. After filtering, the solid product was dissolved in methanol, and the solution was allowed to stand for a while and then 70 wt % *p*-toluene sulfonic acid hydrate (1.2 ml) was added. After removing the solvent, the cyanine dye **3′b** (0.382 g, 47.8%) was obtained by the recrystallization of the solid from water and acetone.

^{1}H NMR (300 MHz, DMSO-*d*): 7.74 (d, $J = 14.1$ Hz, 2H, –CH=), 7.59 (d, $J = 7.2$ Hz, 2H, Ar–H), 7.47–7.35 (m, 6H, Ar–H), 7.26 (m, 2H, Ar–H), 7.09 (d, $J = 8.4$ Hz, 2H, Ar–H), 6.10 (d, $J = 14.1$ Hz, 2H, –CH=), 3.65 (s, 6H, $-CH_3$), 2.93 (m, 4H, $-CH_2-$), 2.27 (s, 3H, $-CH_3$), 1.67 (s, 12H, $-CH_3$); FAB-MS (*m/z*): 470 [M − Ts$^-$]; λ_{max}/nm [ε]: 809 [2.33×10^5].

*2.3.4. 1H-Benz[e]indolium (2-[2-[2-chloro-3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene)ethylidene]-1-cyclohepten-1-yl]ethenyl]-1,1,3-trimethyl) salt with 4-methylbenzenesulfonic acid (chloro indolenine cyanine dye (**3″a**))*

A solution of anilinium salt **1″** (0.465 g, 1.25 mmol), indolenium salt **2a** (1.085 g, 2.75 mmol), 2-propanol (5 ml), acetic anhydride (0.35 ml) and triethylamine (1.05 ml) was stirred at 50 °C for 1 h and to the mixture water (20 ml) was added. After filtering, solid product was dissolved in methanol and the solution was allowed to stand for a while. To the solution 70 wt % *p*-toluene sulfonic acid hydrate (1.2 ml) was added. After removing the solvent the cyanine dye **3″a** (0.612 g, 63.8%) was obtained by the recrystallization of the residue from water and acetone.

^{1}H NMR (300 MHz, DMSO-*d*): 8.41–8.37 (d, $J = 14.4$ Hz, 2H, –CH=), 8.29–8.27 (d, $J = 8.4$ Hz, 2H, Ar–H), 8.07 (t, $J = 9.3$ Hz, 4H, Ar–H), 7.78–7.75 (d, $J = 8.7$ Hz, 2H, Ar–H), 7.64 (t, $J = 8.4$ Hz, 2H, Ar–H), 7.51–7.44 (m, 4H, Ar–H), 7.10–7.08 (d, $J = 7.8$ Hz, 2H, Ar–H), 6.40–6.35 (d, $J = 14.4$ Hz, 2H, –CH=), 3.80 (s, 6H, $-CH_3$), 2.80 (m, 4H, $-CH_2-$), 2.27 (s, 3H, $-CH_3$), 1.94 (s, 12H, $-CH_3$), 1.85–1.83 (m, 4H, $-CH_2-$); FAB-MS (*m/z*): 598 [M − Ts$^-$]; λ_{max}/nm [ε]: 827 [2.56×10^5].

*2.3.5. 3H-Indolium (2-[2-[2-chloro-3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene]-1-cyclohepten-1-yl]ethenyl]-1,3,3-trimethyl) salt with 4-methylbenzenesulfonic acid (chloro indolenine cyanine dye (**3″b**))*

A solution of anilinium salt **1″** (0.465 g, 1.25 mmol), indolenium salt **2b** (0.951 g, 2.75 mmol), 2-propanol (5 ml), acetic

anhydride (0.35 ml) and triethylamine (1.05 ml) was stirred at 50 °C for 1 h and to the mixture water (20 ml) was added. After filtering, the solid product was dissolved in methanol and the solution was allowed to stand for a while. To the solution 70 wt % *p*-toluene sulfonic acid hydrate (1.2 ml) was added. After removing the solvent, cyanine dye **3″b** (0.723 g, 86.4%) was obtained by the recrystallization of the residue from water and acetone.

^{1}H NMR (300 MHz, DMSO-*d*): 8.27 (d, $J = 14.4$ Hz, 2H, −CH═), 7.61 (d, $J = 7.2$ Hz, 2H, Ar−H), 7.47−7.41 (m, 6H, Ar−H), 7.28 (m, 2H, Ar−H), 7.09 (d, $J = 7.8$ Hz, 2H, Ar−H), 6.33 (d, $J = 14.1$ Hz, 2H, −CH═), 3.67 (s, 6H, $-CH_3$), 2.76 (m, 4H, $-CH_2-$), 2.28 (s, 3H, $-CH_3$), 1.79 (m, 4H, $-CH_2-$), 1.65 (s, 12H, $-CH_3$); FAB-MS (*m/z*): 498 [M − Ts$^-$]; λ_{max}/nm [ε]: 787 [3.17×10^5].

2.4. Preparation of barbiturate indolenine cyanine dyes

Barbiturate benzindolenine and indolenine cyanine dyes **4** were synthesized by substituting Cl of meso chloro substituted indolenine cyanine dyes **3** with barbituric acid.

*2.4.1. 1H-Benz[e]indolium (2-[2-[3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene)ethylidene]-2-(hexahydro-1,3-dimethyl-2,4,6-trioxo-5-pyrimidinyl)-1-cyclohexen-1-yl]ethenyl]-1,1,3-trimethyl), inner salt (barbiturate indolenine cyanine dye (**4a**))*

A solution of indolenine cyanine dye **3a** (0.37 g, 0.489 mmol), barbituric acid (0.128 g), methanol (5 ml), triethylamine (0.06 g) and dichloromethane (5 ml) was stirred at 50 °C for 1 h. After removing the solvent, the product was purified by silica gel column chromatography (eluent solvent: chloroform) and cyanine dye **4a** (0.158 g, 54.3%) was obtained.

^{1}H NMR (500 MHz, DMSO-*d*): 8.15 (d, $J = 8.5$ Hz, 2H, Ar−H), 8.0−7.97 (m, 6H), 7.63 (t, $J = 9.0$ Hz, 2H, Ar−H), 7.5 (d, $J = 7.8$ Hz, 2H, Ar−H), 7.4 (t, $J = 7.3$ Hz, 2H, Ar−H), 6.07 (d, $J = 14.5$ Hz, 2H, −CH═), 3.64 (s, 6H, $-CH_3$), 3.20 (s, 6H, $-CH_3$), 2.56 (m, 4H, $-CH_2-$), 1.85 (m, 2H, $-CH_2-$), 1.70 (s, 12H, $-CH_3$); FAB-MS (*m/z*): 703 [M + 1]; λ_{max}/nm [ε]: 787 [2.58×10^5]; IR($\nu_{C=O}$)/cm^{-1}: 1668; Anal. Calcd. for $C_{46}H_{46}N_4O_3 + 3H_2O$: C 72.99, H 6.92, N 7.40, found: C 73.00, H 7.23, N 7.81.

*2.4.2. 3H-Indolium (2-[2-[3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene]-2-(hexahydro-1,3-dimethyl-2,4,6-trioxo-5-pyrimidinyl)-1-cyclohexen-1-yl]ethenyl]-1,3,3-trimethyl) inner salt (barbiturate indolenine cyanine dye (**4b**))*

A solution of indolenine cyanine dye **3b** (0.26 g, 0.400 mmol), barbituric acid (0.128 g), methanol (5 ml), triethylamine (0.06 g) and dichloromethane (5 ml) was stirred at 50 °C for 1 h. After removing the solvent, the product was purified by silica gel column chromatography (eluent solvent: chloroform) and the cyanine dye **4b** (0.0887 g, 49.0%) was obtained.

^{1}H NMR (500 MHz, DMSO-*d*): 7.94 (d, $J = 14.5$ Hz, 2H, −CH═), 7.48 (d, $J = 7.5$ Hz, 2H, Ar−H), 7.32 (t, $J = 7.3$ Hz, 2H, Ar−H), 7.24 (d, $J = 8.0$ Hz, 2H, Ar−H), 7.11 (t, $J = 7.5$ Hz, 2H, Ar−H), 6.02 (d, $J = 14.5$ Hz, 2H, −CH═), 3.52 (s, 6H, $-CH_3$), 3.12 (s, 6H, $-CH_3$), 2.54 (m, 4H, $-CH_2-$), 1.80 (m, 2H, $-CH_2-$), 1.41 (s, 12H, $-CH_3$); FAB-MS (*m/z*): 603 [M + 1]; λ_{max}/nm [ε]: 754 [2.33×10^5]; IR($\nu_{C=O}$)/cm^{-1}: 1671; Anal. Calcd. for $C_{38}H_{42}N_4O_3 + 3H_2O$: C 69.49, H 7.37, N 8.53, found: C 69.14, H 7.45, N 8.23.

*2.4.3. 1H-Benz[e]indolium (2-[2-[3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene)ethylidene]-2-(hexahydro-1,3-dimethyl-2,4,6-trioxo-5-pyrimidinyl)-1-cyclopenten-1-yl]ethenyl]-1,1,3-trimethyl), inner salt (barbiturate indolenine cyanine dye (**4′a**))*

A solution of indolenine cyanine dye **3′a** (0.0616 g, 0.0833 mol), barbituric acid (0.0286 g), methanol (2.5 ml), triethylamine (0.025 g) and dichloromethane (2.5 ml) was stirred at 50 °C for 1 h. After removing the solvent, the product was purified by recrystallization of the residue from water and acetone and the cyanine dye **4′a** (0.0294 g, 47.7%) was obtained.

^{1}H NMR (500 MHz, DMSO-*d*): 8.22−8.20 (d, $J = 8.5$ Hz, 2H, Ar−H), 7.99−7.98 (t, $J = 7.5$ Hz, 4H, Ar−H), 7.76−7.73 (d, $J = 14.0$ Hz, 2H, −CH═), 7.63−7.61 (d, $J = 8.5$ Hz, 2H, Ar−H), 7.54−7.52 (t, $J = 7.5$ Hz, 2H, Ar−H), 7.40−7.39 (t, $J = 7.5$ Hz, 2H, Ar−H), 5.91−5.88 (d, $J = 14.0$ Hz, 2H, −CH═), 3.63 (s, 6H, $-CH_3$), 3.22 (s, 6H, $-CH_3$), 2.84 (m, 4H, $-CH_2-$), 1.79 (s, 12H, $-CH_3$); FAB-MS (*m/z*): 689 [M + 1]; λ_{max}/nm [ε]: 804 [1.74×10^5]; IR($\nu_{C=O}$)/cm^{-1}: 1676; Anal. Calcd. for $C_{45}H_{44}N_4O_3 + 3H_2O$: C 72.25, H 6.78, N 7.54, found: C 72.86, H 6.94, N 6.93.

*2.4.4. 3H-Indolium (2-[2-[3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene]-2-(hexahydro-1,3-dimethyl-2,4,6-trioxo-5-pyrimidinyl)-1-cyclopenten-1-yl]ethenyl]-1,3,3-trimethyl), inner salt (9CI) (barbiturate indolenine cyanine dye (**4′b**))*

A solution of indolenine cyanine dye **3′b** (0.0533 g, 0.0833 mol), barbituric acid (0.0286 g), methanol (2.5 ml), triethylamine (0.025 g) and dichloromethane (2.5 ml) was stirred at 50 °C for 1 h. After removing the solvent, the product was purified by recrystallization of the residue from water and acetoneand the cyanine dye **4′b** (0.0499 g, 75.4%) was obtained.

^{1}H NMR (300 MHz, DMSO-*d*): 7.67−7.62 (d, $J = 14.1$ Hz, 2H, −CH═), 7.47−7.44 (m, 2H, Ar−H), 7.32 (t, $J = 7.4$ Hz, 2H, Ar−H), 7.24−7.21 (d, $J = 8.1$ Hz, 2H, Ar−H), 7.10 (t, $J = 7.1$ Hz, 2H, Ar−H), 5.87−5.82 (d, $J = 13.8$ Hz, 2H, −CH═), 3.50 (s, 6H, $-CH_3$), 3.16 (s, 6H, $-CH_3$), 2.79 (s, 4H, $-CH_2-$), 1.49 (s, 12H, $-CH_3$); FAB-MS (*m/z*): 589 [M + 1]; λ_{max}/nm [ε]: 772 [1.47×10^5]; IR($\nu_{C=O}$)/cm^{-1}: 1681; Anal. Calcd. for $C_{37}H_{40}N_4O_3 + 3H_2O$: C 69.14, H 7.12, N 8.71, found: C 69.50, H 7.53, N 8.69.

*2.4.5. 1H-Benz[e]indolium (2-[2-[3-[(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene)ethylidene]-2-(hexahydro-1,3-dimethyl-2,4,6-trioxo-5-pyrimidinyl)-1-cyclohepten-1-yl]ethenyl]-1,1,3-trimethyl) inner salt (barbiturate indolenine cyanine dye (**4″a**))*

A solution of indolenine cyanine dye **3″a** (0.185 g, 0.240 mol), barbituric acid (0.0390 g), methanol (2.5 ml), triethylamine (0.025 g) and dichloromethane (2.5 ml) was stirred at 50 °C for 1 h. After removing the solvent, the product was

purified by recrystallization of the residue from water and acetone and the cyanine dye **4″a** (0.0493 g, 24.9%) was obtained.

^{1}H NMR (300 MHz, DMSO-*d*): 8.16–8.13 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.98–7.88 (m, 6H), 7.60–7.53 (m, 4H), 7.40–7.36 (d, $J = 7.4$ Hz, 2H, Ar–H), 6.00–5.96 (d, $J = 13.8$ Hz, 2H, –CH=), 3.58 (s, 6H, $-CH_3$), 3.16 (s, 6H, $-CH_3$), 2.66 (m, 4H, $-CH_2-$), 1.79 (m, 4H, $-CH_2-$), 1.71 (s, 12H, $-CH_3$); FAB-MS (*m/z*): 717 [M + 1]; λ_{max}/nm [ε]: 767 [10.1×10^5]; IR($\nu_{C=O}$)/cm^{-1}: 1669; Anal. Calcd. for $C_{47}H_{48}N_4O_3 + 3H_2O$: C 73.22, H 7.05, N 7.26, found: C 73.91, H 6.72, N 7.30.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **3″b**

	x	*y*	*z*	*U*(eq)
S(1)	1570(1)	11 257(1)	2057(1)	56(1)
Cl(1)	3052(1)	5786(1)	4229(1)	58(1)
N(1)	3212(3)	2119(2)	7661(1)	42(1)
N(2)	3275(2)	4986(2)	806(1)	39(1)
C(1)	3728(3)	4127(3)	4220(2)	41(1)
C(2)	4132(3)	3267(3)	4928(2)	42(1)
C(3)	5276(4)	1928(3)	4953(2)	53(1)
C(4)	6281(4)	1753(3)	4239(2)	61(1)
C(5)	5584(4)	1517(3)	3615(2)	67(1)
C(6)	3991(4)	2348(3)	3579(2)	59(1)
C(7)	3772(3)	3768(3)	3537(2)	41(1)
C(8)	3490(3)	3612(3)	5610(2)	43(1)
C(9)	3696(3)	2781(3)	6324(2)	45(1)
C(10)	2978(3)	3034(3)	7007(2)	40(1)
C(11)	1832(3)	4273(3)	7186(2)	43(1)
C(12)	1509(3)	3862(3)	8034(2)	43(1)
C(13)	576(4)	4530(3)	8552(2)	55(1)
C(14)	481(4)	3889(4)	9303(2)	59(1)
C(15)	1299(4)	2617(4)	9541(2)	57(1)
C(16)	2267(4)	1931(3)	9032(2)	51(1)
C(20)	4264(4)	820(3)	7723(2)	59(1)
C(17)	2337(3)	2584(3)	8281(2)	40(1)
C(18)	2471(4)	5407(3)	7012(2)	61(1)
C(19)	447(4)	4651(3)	6764(2)	57(1)
C(21)	3567(3)	4665(3)	2841(2)	40(1)
C(22)	3540(3)	4394(3)	2150(2)	40(1)
C(23)	3301(3)	5314(3)	1465(2)	36(1)
C(24)	3033(3)	6778(3)	1317(2)	38(1)
C(25)	2819(3)	7162(3)	480(2)	42(1)
C(26)	2448(4)	8375(3)	3(2)	57(1)
C(27)	2255(5)	8449(3)	−751(2)	72(1)
C(28)	2429(4)	7362(4)	−1019(2)	65(1)
C(29)	2795(3)	6138(3)	−552(2)	52(1)
C(30)	2976(3)	6082(3)	201(2)	42(1)
C(31)	4369(3)	7083(3)	1479(2)	49(1)
C(32)	1656(3)	7471(3)	1768(2)	46(1)
C(33)	3463(4)	3680(3)	708(2)	49(1)
C(34)	919(3)	10 279(3)	2860(2)	46(1)
C(35)	−216(4)	9845(3)	2798(2)	56(1)
C(36)	−732(4)	9084(3)	3409(2)	61(1)
C(37)	−149(4)	8729(3)	4108(2)	59(1)
C(38)	985(4)	9176(4)	4159(2)	67(1)
C(39)	1519(4)	9938(3)	3546(2)	61(1)
C(40)	−719(5)	7900(4)	4778(2)	85(1)
O(1)	2797(3)	11 474(2)	2273(1)	79(1)
O(2)	2002(4)	10 506(3)	1472(1)	97(1)
O(3)	380(3)	12 391(3)	1861(2)	133(1)
O(4)	4454(4)	702(3)	577(2)	117(1)

U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

*2.4.6. 3H-Indolium (2-[2-[3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene]-2-(hexahydro-1,3-dimethyl-2,4,6-trioxo-5-pyrimidinyl)-1-cyclohepten-1-yl]ethenyl]-1,3,3-trimethyl) inner salt (barbiturate indolenine cyanine dye (**4″b**))*

A solution of indolenine cyanine dye **3″b** (0.160 g, 0.240 mol), barbituric acid (0.0390 g), methanol (2.5 ml),

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **4a**

	x	*y*	*z*	*U*(eq)
N(1)	3912(2)	7476(1)	1357(1)	19(1)
N(2)	−1573(2)	7293(1)	6809(1)	21(1)
N(3)	−123(3)	5803(1)	3912(1)	25(1)
N(4)	2556(3)	5825(1)	4353(1)	24(1)
O(1)	−1508(2)	6538(1)	3590(1)	26(1)
O(2)	1231(2)	5062(1)	4236(1)	37(1)
O(3)	3893(2)	6578(1)	4515(1)	26(1)
C(1)	1140(3)	7195(1)	4057(1)	18(1)
C(2)	1706(3)	7478(1)	3527(2)	20(1)
C(3)	1734(3)	8061(1)	3553(2)	23(1)
C(4)	1705(3)	8269(1)	4302(2)	26(1)
C(5)	376(3)	8025(1)	4584(2)	26(1)
C(6)	517(3)	7444(1)	4609(1)	19(1)
C(7)	2261(3)	7223(1)	2979(1)	21(1)
C(8)	2803(3)	7455(1)	2415(2)	22(1)
C(9)	3447(3)	7212(1)	1894(1)	20(1)
C(10)	3801(3)	6639(1)	1813(1)	19(1)
C(11)	4612(3)	6652(1)	1169(1)	19(1)
C(12)	5312(3)	6256(1)	833(2)	22(1)
C(13)	5301(3)	5726(1)	1011(2)	27(1)
C(14)	6031(3)	5370(1)	669(2)	31(1)
C(15)	6815(3)	5519(1)	126(2)	33(1)
C(16)	6833(3)	6021(1)	−73(2)	28(1)
C(17)	6088(3)	6405(1)	263(2)	22(1)
C(18)	6101(3)	6926(1)	53(2)	24(1)
C(19)	5385(3)	7300(1)	372(1)	20(1)
C(20)	4657(3)	7150(1)	938(1)	19(1)
C(21)	4866(3)	6423(1)	2499(2)	25(1)
C(22)	2264(3)	6334(1)	1621(2)	25(1)
C(23)	3702(3)	8026(1)	1221(1)	22(1)
C(24)	45(3)	7161(1)	5144(1)	19(1)
C(25)	−528(3)	7352(1)	5733(1)	21(1)
C(26)	−1114(3)	7070(1)	6235(1)	19(1)
C(27)	−1457(3)	6491(1)	6249(1)	19(1)
C(28)	−2314(3)	6461(1)	6877(1)	21(1)
C(29)	−3113(3)	6046(1)	7128(2)	24(1)
C(30)	−3213(3)	5542(1)	6844(2)	29(1)
C(31)	−4114(3)	5178(1)	7080(2)	38(1)
C(32)	−4960(3)	5295(1)	7616(2)	41(1)
C(33)	−4842(3)	5767(1)	7927(2)	35(1)
C(34)	−3918(3)	6159(1)	7703(2)	28(1)
C(35)	−3837(3)	6657(1)	8008(2)	30(1)
C(36)	−3052(3)	7048(1)	7762(2)	26(1)
C(37)	−2326(3)	6940(1)	7180(1)	21(1)
C(38)	65(3)	6179(1)	6415(2)	23(1)
C(39)	−2480(3)	6310(1)	5526(1)	23(1)
C(40)	−1431(3)	7842(1)	6980(2)	24(1)
C(41)	1191(3)	6620(1)	4054(1)	18(1)
C(42)	−205(3)	6342(1)	3837(1)	20(1)
C(43)	1220(3)	5532(1)	4173(2)	27(1)
C(44)	2602(3)	6365(1)	4310(1)	20(1)
C(45)	−1559(3)	5497(1)	3737(2)	39(1)
C(46)	4011(3)	5559(1)	4665(2)	39(1)

U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

triethylamine (0.025 g) and dichloromethane (2.5 ml) was stirred at 50 °C for 1 h. After removing the solvent, the product was purified by recrystallization of the residue with water and acetone and the cyanine dye **4″b** (0.0710 g, 48.1%) was obtained.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4″a**

	x	*y*	*z*	*U*(eq)
N(1)	7745(3)	−1903(3)	531(4)	25(1)
N(2)	12 008(3)	3415(3)	5202(4)	25(1)
N(3)	9421(4)	−628(5)	4310(4)	46(2)
N(4)	8939(4)	398(5)	4580(4)	48(2)
O(1)	10 088(3)	−771(3)	3461(3)	36(1)
O(2)	8815(4)	−513(5)	5205(4)	109(3)
O(3)	9064(3)	1299(4)	3933(4)	49(2)
C(1)	9929(4)	564(4)	3064(4)	24(2)
C(2)	9691(4)	81(4)	2318(4)	29(2)
C(3)	10 170(4)	85(5)	1783(4)	29(2)
C(4)	10 990(4)	444(4)	2113(4)	29(2)
C(5)	11 190(4)	1271(5)	2308(5)	36(2)
C(6)	10 645(4)	1589(4)	2634(4)	28(2)
C(7)	10 441(4)	1269(4)	3243(4)	23(1)
C(8)	10 760(4)	1631(4)	3980(4)	22(2)
C(9)	11 261(4)	2349(4)	4248(5)	27(2)
C(10)	11 509(4)	2728(4)	4987(4)	25(2)
C(11)	11 315(4)	2551(4)	5679(4)	21(1)
C(12)	11 784(4)	3222(4)	6282(4)	25(2)
C(13)	11 849(4)	3411(4)	7060(4)	25(2)
C(14)	11 483(4)	2967(5)	7438(5)	34(2)
C(15)	11 546(5)	3188(5)	8178(5)	36(2)
C(16)	11 993(5)	3919(5)	8584(4)	38(2)
C(17)	12 347(5)	4343(4)	8241(5)	35(2)
C(18)	12 297(4)	4135(5)	7457(5)	32(2)
C(19)	12 669(4)	4603(4)	7119(5)	34(2)
C(20)	12 606(4)	4414(4)	6377(5)	30(2)
C(21)	12 163(4)	3720(4)	5963(5)	25(2)
C(22)	12 357(5)	3753(4)	4704(5)	34(2)
C(23)	11 550(4)	1823(4)	5796(5)	28(2)
C(24)	10 476(4)	2454(4)	5635(4)	30(2)
C(25)	8996(4)	−411(4)	2113(4)	23(2)
C(26)	8676(4)	−911(4)	1423(4)	29(2)
C(27)	7996(4)	−1443(4)	1235(5)	27(2)
C(28)	7453(4)	−1632(4)	1695(4)	27(2)
C(29)	6895(4)	−2301(4)	1170(4)	26(2)
C(30)	6263(4)	−2775(5)	1224(5)	31(2)
C(31)	5987(4)	−2656(5)	1895(5)	33(2)
C(32)	5349(5)	−3134(6)	1921(6)	52(3)
C(33)	4979(5)	−3767(5)	1331(7)	52(3)
C(34)	5217(5)	−3898(6)	708(6)	49(3)
C(35)	5872(5)	−3399(5)	641(5)	35(2)
C(36)	6090(5)	−3528(5)	−26(6)	47(2)
C(37)	6728(4)	−3032(4)	−98(4)	25(2)
C(38)	7096(4)	−2439(4)	494(5)	26(2)
C(39)	8103(5)	−1862(5)	−72(4)	35(2)
C(40)	7828(4)	−1815(5)	2407(4)	33(2)
C(41)	7061(5)	−977(4)	1857(5)	40(2)
C(42)	9618(4)	301(4)	3633(4)	27(2)
C(43)	9208(4)	711(5)	4018(4)	36(2)
C(44)	8999(4)	−236(5)	4733(5)	42(2)
C(45)	9723(4)	−396(4)	3762(4)	29(2)
C(46)	9509(6)	−1300(5)	4482(6)	58(2)
C(47)	8518(6)	886(7)	5007(6)	60(3)

U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

^{1}H NMR (300 MHz, DMSO-*d*): 7.85−7.80 (d, $J = 14.4$ Hz, 2H, −CH═), 7.45−7.42 (d, $J = 7.8$ Hz, 2H, Ar−H), 7.29−7.27 (t, $J = 7.8$ Hz, 2H, Ar−H), 7.19−7.16 (d, $J = 7.8$ Hz, 2H, Ar−H), 7.08−7.06 (t, $J = 7.8$ Hz, 2H, Ar−H), 5.96−5.92 (d, $J = 14.4$ Hz, 2H, −CH═), 3.46 (s, 6H, $-CH_3$), 3.10 (s, 6H, $-CH_3$), 2.62 (m, 4H, $-CH_2-$), 1.76 (m, 4H, $-CH_2-$), 1.40 (s, 12H, $-CH_3$); FAB-MS (*m*/*z*): 617 [M + 1]; λ_{max}/nm [ε]: 738 [8.97×10^4]; IR($\nu_{C=O}$)/cm^{-1}: 1673; Anal. Calcd. for $C_{39}H_{44}N_4O_3 + 2H_2O$: C 71.75, H 7.41, N 8.58, found: C 71.56, H 7.39, N 8.61.

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4″b**

	x	*y*	*z*	*U*(eq)
O(1)	4064(1)	6125(1)	4317(1)	22(1)
O(2)	−481(1)	4649(1)	3199(1)	28(1)
O(3)	2013(1)	5415(1)	928(1)	26(1)
N(1)	5099(1)	2158(1)	−122(1)	20(1)
N(2)	3732(2)	10 899(1)	3827(1)	23(1)
N(3)	1747(1)	5545(1)	3752(1)	21(1)
N(4)	784(1)	4996(1)	2060(1)	22(1)
C(1)	4559(2)	6320(1)	2456(1)	18(1)
C(2)	5260(2)	5718(1)	1871(1)	18(1)
C(3)	6550(2)	6274(2)	1616(1)	21(1)
C(4)	7812(2)	6529(2)	2471(1)	25(1)
C(5)	7507(2)	7083(2)	3437(1)	25(1)
C(6)	6629(2)	7919(2)	3307(1)	24(1)
C(7)	5093(2)	7453(1)	2921(1)	20(1)
C(8)	4734(2)	4608(1)	1512(1)	20(1)
C(9)	5205(2)	3904(1)	863(1)	20(1)
C(10)	4572(2)	2823(1)	491(1)	19(1)
C(11)	3216(2)	2196(1)	639(1)	22(1)
C(12)	3079(2)	1120(2)	−48(1)	23(1)
C(13)	2047(2)	201(2)	−292(1)	28(1)
C(14)	2162(2)	−681(2)	−977(1)	33(1)
C(15)	3299(2)	−648(2)	−1409(1)	30(1)
C(16)	4350(2)	269(2)	−1167(1)	26(1)
C(17)	4207(2)	1135(1)	−486(1)	21(1)
C(18)	3361(2)	2068(2)	1716(1)	30(1)
C(19)	1970(2)	2688(2)	327(1)	28(1)
C(20)	6432(2)	2451(2)	−375(1)	25(1)
C(21)	4159(2)	8090(1)	3030(1)	21(1)
C(22)	4424(2)	9216(1)	3407(1)	22(1)
C(23)	3432(2)	9810(1)	3468(1)	21(1)
C(24)	1854(2)	9423(2)	3200(1)	24(1)
C(25)	1387(2)	10 481(2)	3420(1)	27(1)
C(26)	79(2)	10 695(2)	3299(2)	37(1)
C(27)	−67(2)	11 753(2)	3538(2)	40(1)
C(28)	1090(2)	12 578(2)	3895(1)	35(1)
C(29)	2410(2)	12 385(2)	4029(1)	30(1)
C(30)	2536(2)	11 324(2)	3788(1)	24(1)
C(31)	1288(2)	8871(2)	2105(1)	33(1)
C(32)	1362(2)	8705(2)	3880(2)	34(1)
C(33)	5127(2)	11 546(2)	4172(1)	29(1)
C(34)	3192(2)	5841(1)	2607(1)	18(1)
C(35)	3073(2)	5860(1)	3587(1)	18(1)
C(36)	613(2)	5038(1)	3012(1)	21(1)
C(37)	2034(2)	5435(1)	1810(1)	20(1)
C(38)	1561(2)	5728(2)	4771(1)	28(1)
C(39)	−421(2)	4488(2)	1252(1)	33(1)

U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

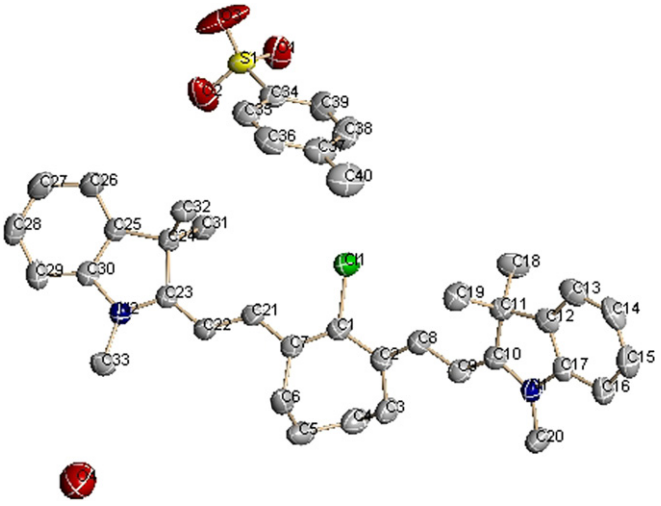


Fig. 1. Molecular structure of **3″b**.

2.5. X-ray crystallographic analysis

Single crystals of **3″a**, **4a**, and **4″a** were obtained from THF and hexane by solvent diffusion, and single crystal of **4″b** was obtained from acetone and water by solvent evaporation. X-ray crystal structure analysis was determined by using Bruker-AXS smart-APEX and analyzed on a SHELXS-97.

X-ray crystal data of **3″a**: Triclinic, $a = 9.7623$ (7), $b = 11.2018$ (8), $c = 18.1825$ (13) Å, $\alpha = 75.891$ (2), $\beta = 81.303$ (2), $\gamma = 70.076$ (2)°, $V = 1807.9$ (2) Å^3, space group = P-1, $Z = 2$, crystal size = $0.50 \times 0.10 \times 0.05$ mm^3, $R_{\text{factor}} = 0.051$.

X-ray crystal data of **4a**: Monoclinic, $a = 8.804$ (2), $b = 26.006$ (6), $c = 18.805(4)$ Å, $\alpha = 90.00$, $\beta = 101.833$ (5), $\gamma = 90.00$°, $V = 4213.7$ (17) Å^3, space group = $P2_1/C$, $Z = 4$, crystal size = $0.50 \times 0.30 \times 0.25$ mm^3, $R_{\text{factor}} = 0.056$.

X-ray crystal data of **4″a**: Triclinic, $a = 19.0024$ (7), $b = 18.9996$ (7), $c = 19.0046$ (8) Å, $\alpha = 101.6160$ (10), $\beta = 101.6010$ (10), $\gamma = 101.6410$ (10)°, $V = 6370.2$ (4) Å^3, space group = P-1, $Z = 6$, crystal size = $0.30 \times 0.30 \times 0.30$ mm^3, $R_{\text{factor}} = 0.060$.

X-ray crystal data of **4″b**: Triclinic, $a = 10.0670$ (10), $b = 12.9212$ (13), $c = 14.1025$ (14) Å, $\alpha = 100.705$ (2), $\beta = 100.211$ (2), $\gamma = 99.917$ (2)°, $V = 1733.6$ (3) Å^3, space group = P-1, $Z = 2$, crystal size = $0.50 \times 0.40 \times 0.40$ mm^3, $R_{\text{factor}} = 0.051$.

The atomic coordinate which was obtained with X-ray crystallography is shown in Tables 1–4.

3. Results and discussion

3.1. Synthesis of barbiturate indolenine cyanine dyes

Anilinium salts **1**, **1′**, and **1″** were obtained by the reaction of cyclohexanone, cyclopentanone, and cycloheptanone with *N*-methylformanilide, respectively. Benzindolenium and indolenium salts **2a**,**b** were obtained by the methylation of benzindolenine and indolenine with methyl *p*-toluene sulfonate, respectively. Chloro indolenine cyanine dyes **3a**, **3′a**,**b**, and **3″a**,**b** were obtained by the reaction of anilinium salts **1**, **1′**, **1″** with indolenium salts **2a**,**b** in the presence of sodium acetate or triethylamine.

Barbiturate indolenine cyanine dyes **4a,b**, **4′a,b**, **4″a,b** were obtained by the chloro substitution reaction of each of the corresponding chloro indolenine cyanine dyes **3a,b**, **3′a,b**, **3″a,b** with barbituric acid in methanol–dichloromethane in the presence of triethylamine, respectively. These barbiturate indolenine cyanine dyes had water in their crystals. The molecular structure due to the X-ray structural analysis of **3″b**, **4a**, **4″a**, **4″b** are shown in Fig. 1–4 respectively. The structure of crystals for these dyes were confirmed and the water content in the crystals of barbiturate indolenine cyanine dyes was identified.

3.2. Absorption spectra of indolenine cyanine dyes

Vis–NIR spectra of chloro indolenine cyanine dye **3a** and barbiturate indolenine cyanine dye **4a** are shown in Fig. 5. These dyes have sharp absorbance peak only in near infrared region. Other chloro indolenine cyanine dyes and barbiturate indolenine cyanine dyes had similar sharp absorption peaks in near infrared region. Maximum wavelength of absorption (max) of barbiturate dyes **4a**,**b**, **4′a**,**b**, **4″a**,**b** and chloro dyes **3a**,**b**, **3′a**,**b**, **3″a**,**b** are shown in Table 5. All barbiturate dyes

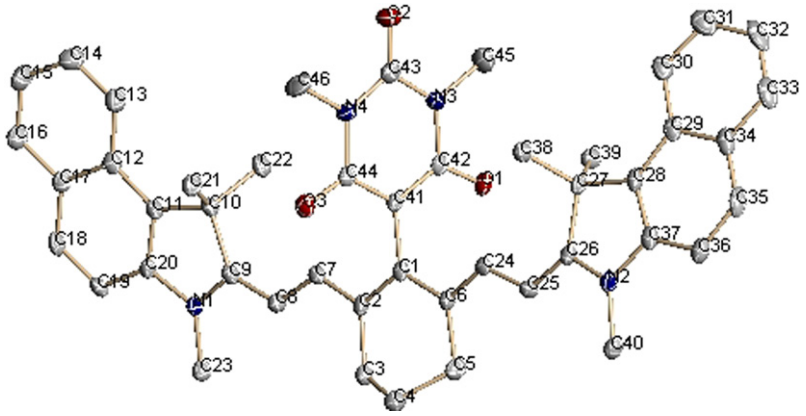


Fig. 2. Molecular structure of **4a**.

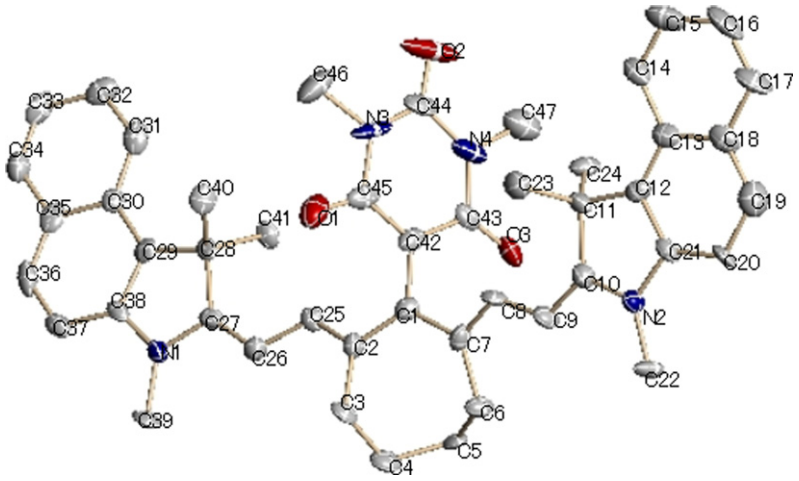


Fig. 3. Molecular structure of **4″a**.

show hypsochromic shift from the corresponding chloro dyes. All barbiturate and chloro benzindolenine dyes show bathochromic shift from each of the corresponding indolenine dyes (barbiturate: 40–41 nm and chloro: 29–33 nm) because of their benzindolenine and indolenine rings difference. Barbiturate benzindolenine and indolenine dyes having six member methine ring (**4a** and **4b**) show 39 and 32 nm hypsochromic shift from the corresponding chloro dyes (**3a** and **3b**). Barbiturate dyes having five member methine ring (**4′a** and **4′b**) show 46 and 37 nm hypsochromic shift from the corresponding chloro dyes (**3′a** and **3′b**). Barbiturate dyes having seven member methine ring (**4″a** and **4″b**) show 60 and 47 nm hypsochromic shift from the corresponding chloro dyes (**3″a** and **3″b**). Thus barbiturate dyes having seven member ring showed the largest hypsochromic shift. The substituent effect at the meso position on absorption of the cyanine dyes is known that the electron-donating group gives hypsochromic effect and electron-withdrawing group gives bathochromic effect. Therefore, the above hypsochromic effect of barbiturate indicates that the electron withdrawing effect of chloro group is larger than that of the barbiturate group. It was understood that all the ^{1}H NMR peaks of protons on the methine chain of barbiturate dyes had shifted all to the high magnetic fields from the corresponding peaks of chloro dyes. But different absorption shifts shown above between the dyes having different methine rings and lower values of barbiturate dyes imply a large steric effect of the barbiturate group.

3.3. Crystal structure of indolenine cyanine dyes

The molecular structure of **3″b** in Fig. 1 shows that the two indolenine rings are distorted. Dihedral angle between the two indolenine ring planes in **3″b** was 38.6°. The molecular structures of **4a** and **4″a** in Fig. 2 and Fig. 3, respectively show that the distortion of the two benzindolenine rings is small but the distortion of the barbiturate is large. The dihedral angles

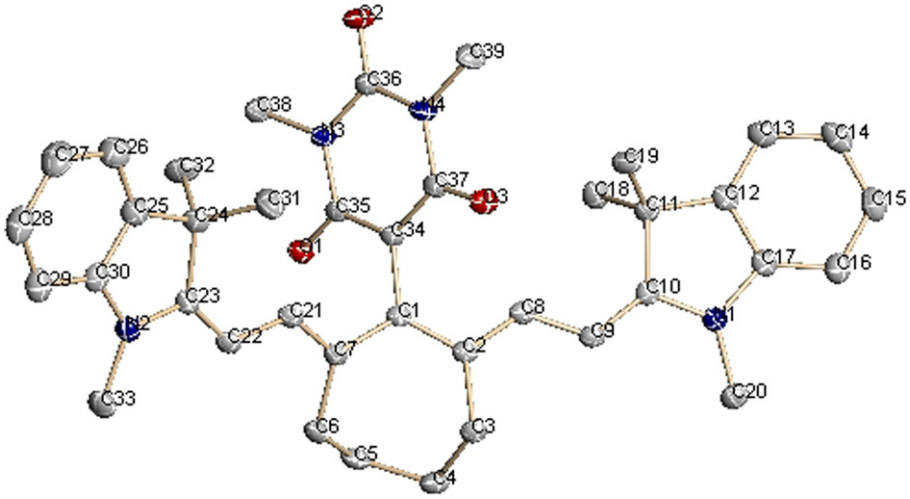


Fig. 4. Molecular structure of **4″b**.

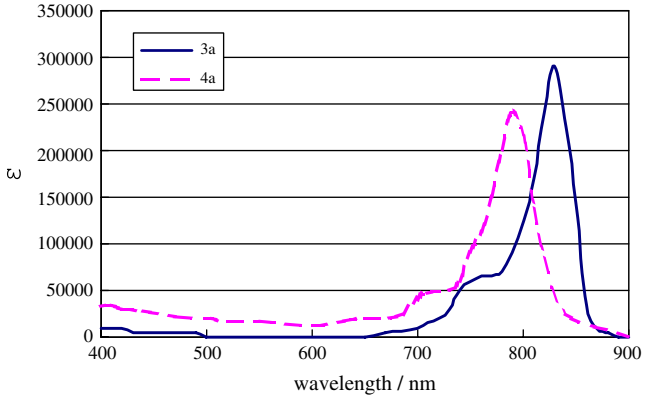


Fig. 5. Vis–NIR spectra of **3a** and **4a** (solvent: CH_2Cl_2).

between barbiturate and two benzindolenine ring, and between two benzindolenine rings were 63.6, 58.0 and 22.4° for **4a** and 70.5, 68.8 and 22.7° for **4″a**. This indicates that barbiturate in **4″a** gives large steric effect from both the benzindolenine rings. The molecular structure of **4″b** in Fig. 4 shows that the two indolenine rings are similarly distorted as in **3″b**. The dihedral angle between two indolenine ring in **4″b** and each dihedral angle between barbiturate and two indolenine rings are 80.1, 53.0 and 38.5°, respectively. Furthermore, the carbon–carbon bond distance between barbiturate and methine chain was longer than other conjugate type carbon–carbon bond distance. The carbon–carbon bond distance between barbiturate and methine chain was 1.48 Å, and carbon–carbon bond distance of methine chain was 1.37–1.41 Å in **4″b**. These indicate that barbiturate ring is sterically hindered by the indolenine ring. It can be presumed that the steric hindrance occurs even in solution since their optimized structure obtained by MOPAC gave similar structure. Consequently, the barbiturate ring was sterically hindered by the indolenine or benzindolenine rings and the barbiturate ring cannot form adequate π-conjugation with the cyanine main chromophore. The barbiturate ring in **4″a** has the largest hindrance and has the most week π-conjugation. Therefore, this barbiturate group has the most week electron-withdrawing effect and gave the largest hypsochromic shift.

Table 5
λ_{max} and ε of Vis–NIR spectra

Dyes	λ_{max}/nm[a] (ε)	Dyes	λ_{max}/nm[a] (ε)
3a	826 (3.23×10^5)	**4a**	787 (2.58×10^5)
3b	786 (3.38×10^5)	**4b**	754 (2.33×10^5)
3′a	850 (3.56×10^5)	**4′a**	804 (1.74×10^5)
3′b	809 (2.33×10^5)	**4′b**	772 (1.47×10^5)
3″a	827 (2.56×10^5)	**4″a**	767 (1.01×10^5)
3″b	787 (3.17×10^5)	**4″b**	738 (8.97×10^4)

[a] Solvent: CH_2Cl_2.

4. Conclusion

Barbiturate indolenine and benzindolenine cyanine dyes were synthesized. These dyes had absorption near 800 nm and all barbiturate dyes showed hypsochromic shift from the corresponding chloro dyes. The crystal structure of barbiturate dyes indicates that the barbiturate ring is sterically hindered by the indolenine ring.

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