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Synthesis of 4-Substituted Bisnaphthalimides

D.G. Kupriyan[1], V.F. Anikin[1], A. Merz[2], and L.D. Pantsenker[3]

[1] *Mechnikov Odessa National University, Odessa, 65026 Ukraine; e-mail: anikin@paco.odessa.ua*
[2] *Organisch-chemisches Institut von Universitaet Regensburg, BRD*
[3] *Institute of Single Crystals, National Academy of Sciences of Ukraine, Ukraine*

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Abstract—The synthetic route to 4-substituted bisnaphthalimides consisting in reaction of 4-halonaphthalic anhydrides with α,ω-diaminoalkanes followed by halogen substitution with dialkylamino group is more promising than imidating coupling of 4-dialkylaminonaphthalic anhydrides for it opens wider synthetic opportunities and ensures better yields of target products. Dihalosubstituted bis-naphthalimides can be prepared by N-alkylation of the corresponding naphthalimides with polymethylene dibromides under conditions of phase-transfer catalysis in the presence of tetraalkylammonium salts.

Naphtalic acid derivatives attract interest as promising pharmaceuticals [1–5]. Therewith the efficient in, e.g., suppressing tumor growth has proved bisnaphthalimides, compounds where the nitrogen atoms of two naphthalene structures are connected by a polymethylene or oxa(aza)polymethylene chain [6, 7]. Mononaphthalic compounds are also widely used as fluorescent dyes for polymer materials, labels and probes in medical and biological research, dyes for lasers, and as analytical reagents [8–11]. The presence of an electron-donor substituent in position *4* of the naphthalic moiety results in sharp increase in the luminescence and in significant longwave shift of the absorption and fluorescence bands [8]. Up till now bisnaphthalimides with electron-donor substituents were unknown.

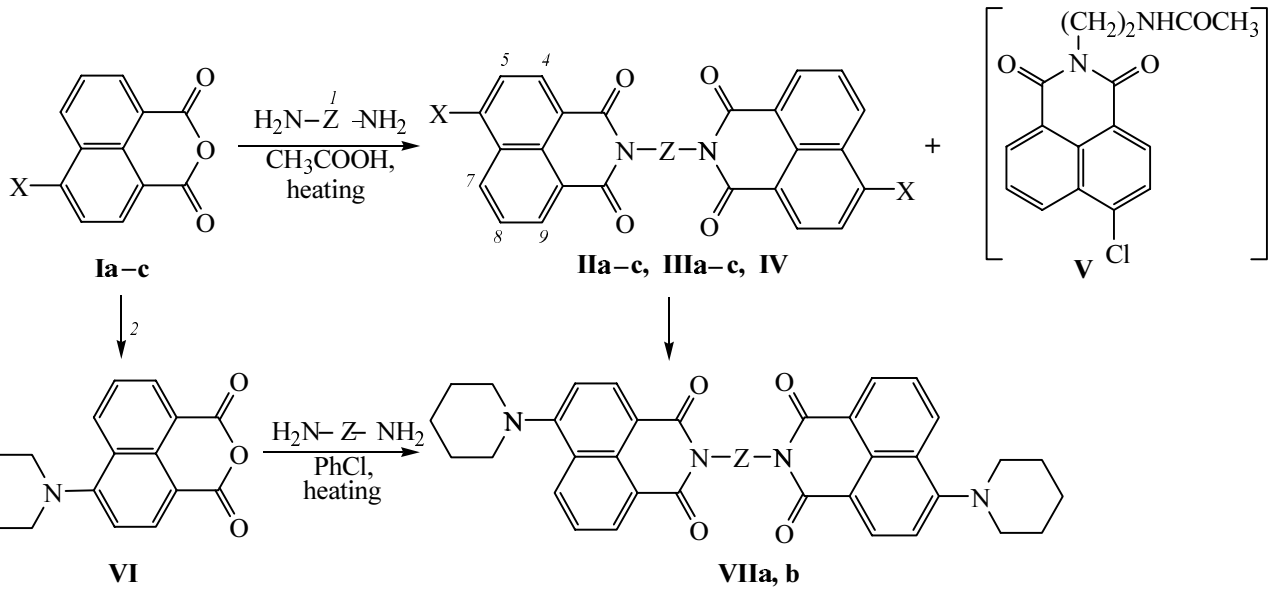
Aiming at development of optimum approach to the synthesis of these compounds we considered alternative versions of building up bisnaphthalimide molecules. As model compounds were selected 4-chloro- (**Ia**), 4-bromo- (**Ib**), and 4-nitronaphthalic (**Ic**) anhydrides that were bound by imidation with ethylenediamine, hexamethylenediamine, and 3-oxapentane-1,5-diamine.

The general procedure for preparation of bisnaphthalimides consists in acylation of the appropriate diamines with naphthalic (commonly 3-amino- and 3-nitronaphthalic) anhydrides [6, 7]. Two paths are possible for preparation of bisnaphthalimides from a diamine and naphthalic anhydride **I**. The first one (path *1*), for instance, with 4-chloronaphthalic anhydride (**Ia**), consists in succession **Ia** – 4,4'-dichlorobisnaphthalimide (**IIa**) – 4-(*N,N*-dialkyl-amino)bisnaphthalimide (**VIIa**), path *2* involves a succession **(Ia)** – 4-(*N,N*-dialkylamino)-naphthalic anhydride **(VI)** – 4-(*N,N*-dialkylamino)bisnaphthalimide **(VIIa)** (Scheme 1). Despite the equal number of stages the first way to bisnaphthalimides appears as more valuable for it provides a possibility of subsequent replacement of chlorine by versatile alkylamino, dialkylamino, and alkoxy groups. As to the second procedure, here the range of final bisnaphthalimides is determined by the available set of naphthalic anhydrides that contain in the aromatic ring only the secondary amino groups and heterocyclic fragments [12, 13]. The use in this process of 4-alkylamino-naphthalic anhydrides seems hardy probable. For instance, by an example of 4,5-dichloronaphthalic anhydride we observed formation of 4-alkylamino derivatives, but in a low yield [14]; the aminolysis of 4-substituted compounds with primary amines failed to afford these substances [15].

The chromatographic analysis of reaction products obtained from hexamethylenediamine and anhydride **Ia** in various solvents (chlorobenzene, methanol, ethanol, pyridine, acetic acid) showed that only the use of acetic acid suppressed the formation of substitution products. The boiling of a mixture of the diamine and the anhydride in acetic acid for 50 h afforded bisnaphthalimides **II** or **III** that after one recrystallization turned out to be chromatographically pure substances. By this procedure we prepared a series of six bisnaphthalimides **II** and **III**. All compounds possess strong absorption bands in UV region, but no fluorescence is observed.

^{1}H NMR spectra confirm the structure of synthesized bisnaphthalimides **II** and **III**. The aromatic protons signals are observed in the region 7.0–8.6 ppm; protons H^4

Scheme 1.



I, X=Cl (**a**), Br (**b**), NO_2 (c); **II**, Z= -$(CH_2)_6$- : X=Cl (**a**), Br (b), NO_2 (**c**); **III**, Z= -$CH_2CH_2OCH_2CH_2$- : X= Cl (**a**), Br (**b**), NO_2 (**c**); **IV**, Z= -$(CH_2)_2$-, X=Cl; **VII**, Z= -$(CH_2)_6$- (**a**), -$CH_2CH_2OCH_2CH_2$- (**b**).

and H^5 appear as doublets, H^8 as a quartet due to coupling with magnetically nonequivalent protons H^7 and H^9 observed as doublet signals. The spin-spin coupling constants have values characteristic of napthalimide derivatives. The position of aliphatic proton signals and their splitting distinguish the spectra of bisimides containing hexamethylene (**II**) and 3-oxapenta-1,5-diyl (**III**) fragments.

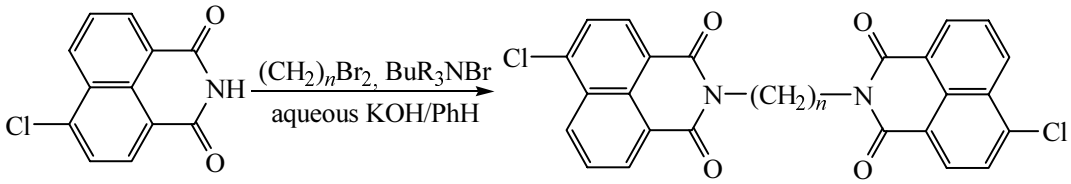
We demonstrated the opportunity of further modification of synthons obtained by an example of halogen replacement in the chlorine-containing bisnaphthalimides. We selected piperidine as a nucleophilic reagent for introducing donor substituent. Piperidine is a highly basic amine, and its introduction into a naphthalimide structure is known to afford compounds with yellow-green luminescence [10, 12]. The reaction was carried out in chlorobenzene at a 10-fold excess of the amine. Thus bisnaphthalimides **VII** were obtained containing 4-piperidino group and bridging moieties generated from hexamethylenediamine and 3-oxapentane-1,5-diamine. Along path *2*, namely, by acylating diamines with anhydride **VI**, bisnaphthylimides **VII** were obtained in a lower yield.

It should be remarked that the acylation of ethylenediamine with 4-chloronaphthalic anhydride (**Ia**) afforded the target bisnaphthalimide **IV** in a low yield, but the reaction simultaneously gave rise to another product which according to IR, ^{1}H NMR and mass spectra was identified as 2-(2-acetylaminoethyl)-6-chloro-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione (**V**). Its boiling in acetic acid in the presence of 4-chloronaphthalic anhydride (**Ia**) did not result in formation of bisimide **IV**. Inasmuch as no transamidation of compound **V** occurred under these conditions even at prolonged heating, compound **V** could not be an intermediate in formation of imide **IV**.

We showed formerly that naphthalimide was efficiently alkylated with alkyl halides under conditions of the phase-transfer catalysis in the presence of tetraalkylammonium salts [16]. The possibility of preparation of bisnaphthalimides by this method should have been tested. As initial compounds we chose 4-chloronaphthalimide (**VIII**), polymethylene dibromides, and a phase-transfer catalyst butyltrialkylammonium bromide [16]. The syntheses under comparable conditions revealed the dependence of the target product yield on the chain length of the polymethylene dibromide. For instance, in the mixture of 4- chloronaphthalimide (**VIII**) with 1,2-dibromoethane formed no bisimide **IV**, and the use of 1,3-dibromopropane resulted in 24% yield of bisimide **IXa**. The highest yields were obtained with tetra-, penta-, and hexamethylene dibromides (Scheme 2). The structure of compounds **IX** was confirmed by ^{1}H NMR spectra.

It is worth noting in conclusion that synthesized halo- and nitro-substituted bisnaphthalimides are convenient synthones for preparation of new class luminophores. The feasibility of bisnaphthalimides preparation along the route **Ia** – 4,4'-dichlorobisnaphthalimide (**IIa**) – 4-(*N,N*-dialkylamino)bisnaphthalimide is proved experimentally.

Scheme 2.



VIII **IIa, IXa–c**

The preparation of bisnaphthalimides was shown to be possible by alkylation of substituted naphthalimides with polymethylene dibromides under conditions of the phase-transfer catalysis. The study of luminescent spectra of compounds obtained will be the subject of our subsequent paper.

EXPERIMENTAL

IR spectra of compounds were registered on spectrophotometer Mattson FTIR 1001 from KBr pellets. ^{1}H NMR spectra were registered on spectrometers Bruker WM 250 and Bruker WM 400 from solutions in $CDCl_3$, internal reference TMS. UV spectra of solutions in chloroform were recorded on spectrophotometer Specord UV-VIS. Mass spectra were measured on a mass spectrometer Varian MAT 311A, ionizing electrons energy 70 eV, ionizing chamber temperature 200°C, direct admission into the ionizing chamber. The reaction progress was monitored and the purity of compounds synthesized was checked by TLC on Silica gel 60 F_{254} (Merck) plates, development under UV irradiation. Solvents were purified by procedures from [17]. The initial halo- and nitronaphthalic anhydrides **Ia**–**c** were prepared as in[18–20], 4-chloronaphthalimide (**VIII**) was obtained by method [21]. Butyltrialkylammonium bromide was obtained by alkylating with butyl bromide in DMF by procedure [16] a crude mixture of trialkylamines of mean molecular weight 370 (alkyl groups contained 7–9 carbon atoms).

2,2'-(Hexamethylene)bis[6-chloro-1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione] (IIa). A solution of 2.4 g (10.3 mmol) of anhydride **Ia** and 0.58 g (5.0 mmol) of hexamethylenediamine in 100 ml of glacial acetic acid was boiled for 53 h. To remove the side products containing free amino groups 30 ml of 10% hydrochloric acid was added to the reaction mixture, and it was boiled for 40–50 min. The cooled reaction mixture was diluted with 4 volumes of water, the precipitate formed was filtered off and washed till neutral washings. To remove the unreacted initial anhydride the product obtained was boiled for 1 h with 50 ml of 3% sodium carbonate solution, the precipitate was filtered off, washed with water, and dried for 2 h at 120°C. We obtained 2.45 g of reaction product. After one crystallization thereof 1.8 g (66%) of chromatographically pure compound **IIa** was obtained as colorless crystals, mp 265–266.5°C (acetic acid). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) : 1.46–1.85 m (8H, $4CH_2$); 4.17 t (4H, NCH_2, 7.5); 8.48 d (2H, H^4, 7.6); 7.81 d (2H, H^5, 7.6); 8.59 d (2H, H^7, 8.4); 7.84 q (2H, H^8, 8.4, 7.4); 8.62 d (2H, H^9, 7.4). UV spectrum, λ_{max}, nm (log ε) : 329 (4.37), 344 (4.5), 359 (4.46). Found, %: C 65.94, 66.13; H 4.08, 4.15; N 5.10, 5.16. $C_{30}H_{22}Cl_2N_2O_4$. Calculated, %: C 66.06; H 4.07; N 5.13.

2,2'-(Hexamethylene)bis[6-bromo-1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione] (IIb) was prepared similarly to compound **IIa** from 2.9 g (10.5 mmol) of anhydride **Ib,** 0.58 g (5.0 mmol) of hexamethylenediamine, and 110 ml of glacial acetic acid. We obtained 2 g (63%) of compound **IIb** as colorless crystals, mp. 280–281.5°C (acetic acid). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.42–1.82 μ (8H, $4CH_2$); 4.17 t (4H, NCH_2, 7.6); 8.38 d (2H, H^4, 7.7); 8.03 d (2H, H^5, 7.7); 8.56 d (2H, H^7, 8.5); 7.83 q (2H, H^8, 8.5, 7.4); 8.63 d (2H, H^9, 7.4). UV spectrum, λ_{max}, nm (log ε): 328 (4.40), 344 (4.57), 360 (4.50). Found, %: C 57.00, 56.94; H 3.60, 3.65; N 4.62, 4.58. $C_{30}H_{22}Br_2N_2O_4$. Calculated, %: C 56.81; H 3.50; N 4.41.

2,2'-(Hexamethylene)bis[6-nitro-1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione] (IIc). Likewise compound **IIc** was obtained from 1.23 g (5.1 mmol) of anhydride **Ic**, 0.29 g (2.5 mmol) of hexamethylenediamine, and 60 ml of glacial acetic acid. We obtained 0.9 g (64%) of compound **IIc** as light-yellow crystals, mp. 290–292°C (acetic acid). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.45–1.83 m (8H, $4CH_2$); 4.19 t (4H, NCH_2, 7.5); 8.67 d (2H, H^4, 7.8); 8.40 d (2H, H^5, 7.8); 8.84 d (2H, H^7, 8.1); 7.98 q (2H, H^8, 8.1, 7.0); 8.63 d (2H, H^9, 7.0). UV spectrum, λ_{max}, nm (log ε): 353 (4.42). Found, %: C 63.49, 63.61; H 4.08, 4.00; N 9.85, 9.91. $C_{30}H_{22}N_4O_8$. Calculated, %: C 63.61; H 3.91; N 9.88.

2,2'-(3-Oxapentamethylene)bis[6-chloro-1*H*-benz-[*de*]isoquinoline-1,3(2*H*)-dione] (IIIa). A solu-

tion of 2.4 g (10.3 mmol) of anhydride **Ia** and 0.52 g (5.0 mmol) of 2,2'-diaminodiethyl ether in 100 ml of glacial acetic acid was boiled for 55 h. The workup of the reaction mixture and isolation of the final product was performed as in the case of compounds **II**. We separated 2.4 g of reaction product that on crystallization afforded 1.65 g (62%) of chromatographically pure imide **IIIa** as colorless crystals, mp. 241–242.5°C (acetic acid). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.89 t (4H, NCH_2, 5.4); 4.37 t (4H, OCH_2, 5.4); 8.03 d (2H, H^4, 8.0); 7.88 d (2H, H^5, 8.0); 8.50 d (2H, H^7, 8.4); 7.70 q (2H, H^8, 8.4, 7.4); 8.28 d (2H, H^9, 7.4). UV spectrum, λ_{max}, nm (log ε): 329 (4.40), 343 (4.50), 359 (4.41). Found, %: C 63.12, 62.15; H 3.45, 3.49; N 5.27, 5.30. $C_{28}H_{18}Cl_2N_2O_5$. Calculated, %: C 63.05; H 3.40; N 5.25.

2,2'-(3-Oxapentamethylene)bis[6-bromo-1*H*-benz-[*de*]isoquinoline-1,3(2*H*)-dione] (IIIb) was obtained in the same way as compound **IIIa** from a solution of 2.9 g (10.5 mmol) of anhydride **Ib** and 0.52 g (5.0 mmol) of 2,2'- diaminodiethyl ether in 110 ml of glacial acetic acid. We obtained 2 g (65%) of compound **IIIb** as colorless crystals, mp 252.5–254.5°C (acetic acid). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.88 t (4H, NCH_2, 5.4); 4.37 t (4H, OCH_2, 5.4); 8.15 d (2H, H^4, 7.8); 7.67 d (2H, H^5, 7.8); 8.53 d (2H, H^7, 8.4); 7.71 q (2H, H^8, 8.4, 7.4); 8.32 d (2H, H^9, 7.4). UV spectrum, λ_{max}, nm (log ε): 329 (4.40), 343 (4.50), 360 (4.44). Found, %: C 53.95, 54.06; H 3.04, 3.08; N 4.75, 4.79. $C_{28}H_{18}Br_2N_2O_5$. Calculated, % C 54.04; H 2.92; N 4.50.

2,2'-(3-Oxapentamethylene)bis[6-nitro-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione] (IIIc) was obtained in the same way as compound **IIIa** from a solution of 1.23 g (5.1 mmol) of anhydride **Ic** and 0.26 g (2.5 mmol) of 2,2'- diaminodiethyl ether in 50 ml of glacial acetic acid. We obtained 0.8 g (58%) of compound **IIIc** as golden plates, mp 227–228.5°C (acetic acid). ^{1}H NMR spectrum, δ, ppm (*J*, Hz) : 3.90 t (4H, NCH_2, 5.3); 4.39 t (4H, OCH_2, 5.3); 8.38 d (2H, H^4, 8.1); 8.27 d (2H, H^5, 8.1); 8.74 d (2H, H^7, 8.7); 7.86 q (2H, H^8, 8.7, 7.4); 8.35 d (2H, H^9, 7.4). UV spectrum, λ_{max}, nm (log ε): 351 (4.35). Found, %: C 60.46, 60.52; H 3.30, 3.36; N 10.35, 10.28. $C_{28}H_{18}N_4O_9$. Calculated, %: C 60.65; H 3.27; N 10.10.

2,2'-(Ethylene)bis[6-chloro-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione] (IV) and 2-(2-acetylaminoethyl)-6-chloro-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione (V). A mixture of 2.4 g (10.3 mmol) of 4-chloronaphthalic anhydride **Ia** and 0.3 g (5 mmol) of ethylenediamine in 100 ml of glacial acetic acid was boiled for 40 h. Then the reaction mixture was diluted with 9 volumes of water, the separated precipitate was filtered off, charged into a flask, and boiled with 100 ml of 3% sodium carbonate solution to remove the excess initial anhydride. The residue was filtered off, washed with water, and dried for 1 h at 120°C. We obtained 1.1 g of substance that according to TLC data (eluent acetone–hexane, 2 :3) was a mixture of several compounds. In order to separate the components the mixture obtained was boiled for 2 min with 50 ml of methanol and filtered hot. On cooling the solution we separated precipitate of 0.4 g (25%) of chromatographically pure compound identified as 2-(2-acetylaminOethyl)-6-chloro-1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione (**V**), mp 201.5–203°C (methanol). The fraction insoluble in methanol consisted of 2,2'-(ethylene)bis[6-chloro-1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione] (**IV**). We obtained 0.6 g (25%) of compound **IV** as colorless crystals, mp 410–412°C. IR spectra, ν, cm^{-1}: **IV**, 1090, 1235, 1365, 1435, 1590, 1670 (C=O), 1700 (C=O), 3095. **V**, 1060, 1235, 1375, 1435, 1590, 1660 (C=O), 1705 (C=O), 2920. ^{1}H NMR spectra (CF_3COOD), δ, ppm (*J*, Hz): **IV**, 4.92 s (4H, NCH_2); 8.53 d (2H, H^4, 8.0); 7.92 d (2H, H^5, 8.0); 8.86 d (2H, H^7, 8.6); 7.94 q (2H, H^8, 8.6, 7.4); 8.68 d (2H, H^9, 7.4). **V**, 1.90 s (3H, CH_3); 3.67 m (2H, CH_2); 4.39 t (2H, NCH_2, 5.6); 6.20 s (1H, NH); 8.51 d (1H, H^4, 7.9); 7.83 d (1H, H^5, 7.9); 8.62 d (1H, H^7, 8.6); 7.87 q (1H, H^8, 8.6, 7.1); 8.67 d (1H, H^9, 7.1). UV spectra, λ_{max}, nm (log ε): **IV**, 329 (4.39), 343 (4.46), 360 (4.41). **V**, 329 (4.10), 345 (4.18), 360 (4.12). Mass spectra, *m/z* (I_{rel}, %): **IV**, 490(27), 489(11), 488(40) $[M]^+$, 259(30), 258(28), 257(100), 256(48), 246(11), 244(39), 231(15), 216(12), 214(39), 188(29), 187(12), 186(18), 161(10), 160(15), 31(13), 29(10). **V**, 316(21) $[M]^+$, 258(10), 257(23), 256(14), 247(29), 246(23), 245(94), 244(35), 234(28), 233(17), 232(88), 231(19), 217(22), 216(15), 214(36), 189(13), 188(26), 187(12), 186(22), 161(17), 160(22), 126(18), 125(11), 85(100), 43(44), 30(34). Found, % **IV**: C 63.85, 63.80; H 2.80, 2.86; N 5.68, 5.70. $C_{26}H_{14}Cl_2N_2O_4$. Calculated, %: C 63.93; H 2.86; N 5.73. Found, % **V**: C 60.68, 60.74; H 4.07, 4.10; N 8.80, 8.82. $C_{16}H_{13}ClN_2O_3$. Calculated , %: C 60.76; H 4.11; N 8.86.

4-Piperidinonaphthalic anhydride (VI). A solution of 2.76 g (10.0 mmol) of anhydride **Ib** and 1.7 g (20.0 mmol) of piperidine in 100 ml of chlorobenzene was boiled till complete consumption of the initial anhydride (for10 h). The chlorobenzene was removed by steam-distillation, and the reaction product was extracted with chloroform. The extract was dried with calcium chloride, chloroform was evaporated to furnish 2.75 g of the crude reaction product that on crystallization provided 2.2 g (78%) of chromatographically pure compound **VI** as bright orange crystals, mp 176–177.5°C (2-propanol) (publ.: mp 168–170°C [12]).

2,2'-(Hexamethylene)bis[6-piperidino-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione] (VIIa). (a) In 5 ml of chlorobenzene was dissolved 0.2 g (0.37 mmol) of hexamethylene)bis[6-chloro-1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione] (**IIa**). To the solution obtained was added 0.62 g(7.2 mmol) of piperidine. The reaction mixture was boiled for 36 h till complete conversion of the initial bisimide and the intermediate monosubstituted product. The obtained mixture was treated with 10% hydrochloric acid, washed with water, and the chlorobenzene was evaporated. The target product was isolated by column chromatography on silica gel (eluent chloroform–acetone, 20:1). We obtained 0.21 g (89%) of bisimide **VIIa** as bright yellow crystals, mp 256–258°C.

(b) To a solution of 0.29 g (1.03 mmol) of 4-piperidinonaphthalic anhydride (**VI**) in 10 ml of chlorobenzene was added 0.058 g (0.5 mmol) of hexamethylenediamine. The reaction mixture was boiled for 85 h. The excess initial anhydride **VI** was separated by stirring the reaction mixture with 15% sodium hydroxide solution for 1 h, the organic phase was washed with water, and chlorobenzene was evaporated.The target product was isolated by column chromatography on silica gel. We obtained 0.12 g (38%) of 2,2'-(hexamethylene)bis[6-piperidino-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione] (**VIIa**) as bright yellow crystals, mp 256–258°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.4–2.0 m (20H, CH_2 groups of hexamethylene and piperidine fragments); 3.23 m (8H, NCH_2 of piperidine); 4.15 t (4H, NCH_2, 7.5); 8.48 d (2H, H^4, 8.1); 7.18 d (2H, H^5, 8.1); 8.40 d (2H, H^7, 8.3); 7.67 q (2H, H^8, 8.3, 7.5); 8.55 d (2H, H^9, 7.5). UV spectrum, λ_{max}, nm (log ε): 260 (4.57), 280 (4.36), 343 (3.77), 412 (4.41). Found, %: C 74.68, 74.59; H 6.60, 6.65; N 8.57, 8.60. $C_{40}H_{42}N_4O_4$. Calculated, %: C 74.74; H 6.59; N 8.72.

2,2'-(3-Oxapentamethylene)bis[6-piperidino-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione] (VIIb). (a) Bisimide **VIIb** was prepared similarly to the preceding luminophore **VIIa** from 0.2 g (0.38 mmol) of compound **IIIa** in 5 ml of chlorobenzene and 0.64 g (7.6 mmol) of piperidine. The process was carried out for 36 h to obtain 0.21(89%) of 2,2'-(3-oxapentamethylene)bis-[6-piperidino-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione] **VIIb** as bright orange crystal (eluent for chromatography benzene–ethyl acetate, 2:1), mp 216–218°C.

(b) Similarly to preparation of compound **VIIa** (method b) from 0.29 g (1.03 mmol) of 4-piperidinonaphthalic anhydride **VI** dissolved in 8 ml of chlorobenzene and 0.054 g (0.5 mmol) of 2,2'-diaminodiethyl ether was obtained 0.13 g (41%) of 2,2'-(3-oxapentamethylene)bis[6-piperidino-1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione], mp 217–219°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.65–2.0 m (12H, CH_2 groups of piperidine); 3.23 m (8H, NCH_2 of piperidine); 3.86 t (4H, NCH_2, 5.9); 4.39 t (4H, OCH_2, 5.9); 8.29 d (2H, H^4, 8.1); 7.10 d (2H, H^5, 8.1); 8.40 d (2H, H^7, 8.4); 7.59 q (2H, H^8, 8.4, 7.3); 8.35 d (2H, H^9, 7.3). UV spectrum, λ_{max}, nm (log ε): 260 (4.60), 281 (4.39), 343 (3.81), 409 (4.44). Found, %: C 72.12, 72.20; H 6.10, 6.15; N 9.00, 9.06. $C_{38}H_{38}N_4O_5$. Calculated, %: C 72.36; H 6.07; N 8.88.

2,2'-(Trimethylene)bis[6-chloro-1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione] (IXa), 2,2'-(tetramethylene)bis[6-chloro-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione] (IXb), 2,2'-(pentamethylene)bis[6-chloro-1*H*-benz[*de*]isoquinoline-1,3(2*H*)-dione] (IXc), 2,2'-(hexamethylene)bis[6-chloro-1*H*-benz[*de*]isoquinoline-1,3-(2*H*)-dione] (IIa). To a solution of 0.03 g (0.007 mmol) of butyltetraalkylammonium bromide in 20 ml of benzene was added 0.5 g (2.15 mmol) of finely ground 4-chloronaphthylimide (**VIII**), 10 ml of 10% water solution of potassium hydroxide, and 1.08 mmol of an appropriate polymethylene dibromide. The reaction mixture was boiled at vigorous stirring for 4 h. In the event the products were sparingly soluble in benzene (**IXa, b**) the reaction mixture was cooled to 20°C, the precipitated crystals were filtered off, washed with water and ethyl ether, and crystallized from acetic acid. To isolate compounds **IXc** and **IIa** after completion of the reaction 20 ml of benzene was added to the reaction mixture, and it was brought to boiling. The benzene layer was separated without cooling, and then it was twice washed with water. The benzene was evaporated, and the solid residue obtained was dissolved in acetic acid and boiled for 10 min with activated carbon. The solution was filtered while hot. On cooling the precipitated crystals were filtered off, washed with acetic acid and ethyl ether to give 0.3 g (53%) of compound **IIa**, mp 265–267°C (acetic acid); 0.13 g (24%) of compound **IXa**, mp 314–316°C (acetic acid); 0.3 g (53%) of compound **IXb**, mp 305–306°C (acetic acid); 0.29 g (51%) of compound **IXc**, mp 228–230°C (acetic acid). The isolated compounds **IIa**, **IXa–c** are colorless crystals. ^{1}H NMR spectra (CF_3COOD), δ, ppm (*J*, Hz): **IXa,** 2.42 q (2H, CH_2); 4.51 t (4H, NCH_2); 8.52 d (2H, H^4, 8.1); 7.83–7.95 m (4H, H^5+H^8); 8.76 d (2H, H^7, 8.5); 8.70 d (2H, H^9, 7.3). **IXb**, 2.10 m [4H, $(CH_2)_n$]; 4.45 m (4H, NCH_2); 8.61 d (2H, H^4, 8.1); 7.93 d (2H, H^5, 8.1); 8.83 d (2H, H^7, 8.5); 7.96 q (2H, H^8, 8.5, 7.3); 8.77 d (2H, H^9, 7.3). **IXc**, 1.6–2.0 m (6H, $3CH_2$); 4.39 t (4H, NCH_2, 7.7); 8.61 d (2H,

H^4, 8.1); 7.93–8.0 m (4H, H^5+H^8); 8.85 d (2H, H^7, 8.3); 8.78 d (2H, H^9, 7.3). UV spectra, λ_{max}, nm (log ε): **IXa**, 330 (4.38), 343 (4.46). **IXb**, 330 (4.38), 344 (4.48), 359 (4.44); **IXc**, 329 (4.4), 344 (4.5), 359 (4.46). Found, % **IXa**: C 64.48, 64.52; H 3.12, 3.16; N 5.49, 5.54. $C_{27}H_{16}Cl_2N_2O_4$. Calculated, %: C 64.54; H 3.19; N 5.58. Found, % **IXc**: C 65.00, 65.08; H 3.44, 3.51; N 5.37, 5.40. $C_{28}H_{18}Cl_2N_2O_4$. Calculated, %: C 65.12; H 3.49; N 5.43. Found, % **IXc**: C 65.58, 65.60; H 3.68, 3.72; N 5.20, 5.23. $C_{29}H_{20}Cl_2N_2O_4$. Calculated, %: C 65.66; H 3.77; N 5.28.

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