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Synthesis and Fluorescence of Anthra[2,3-*b*]furan-5,10-dione Derivatives

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Abstract—4,11-Dialkoxyanthra[2,3-*b*]furan-5,10-diones containing various substituents in the 3-position were synthesized. Reactions of these compounds with primary and secondary amines resulted in nucleophilic replacement of one or two alkoxy groups by the corresponding amine residues. 4,11-Dialkoxy derivatives of anthra[2,3-*b*]furan-5,10-dione showed fluorescence with large Stokes shifts (170–200 nm).

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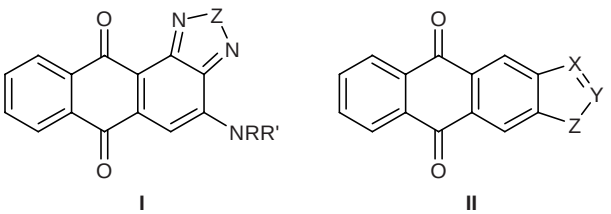
Aromatic and heteroaromatic compounds exhibiting strong fluorescence find new applications in practice as probes for studying biochemical processes [1] and materials for data recording, storage, and reproduction [2]. 9,10-Anthraquinone derivatives containing amino or hydroxy groups possess fluorescent properties [3]; however, their fluorescence intensity is not high. Fusion of a heteroaromatic ring to anthraquinone considerably changes its spectral parameters. For example, angular hetarenoanthraquinones like **I** are red or violet, and they show strong fluorescence in the long-wave region [4]. Some linearly fused hetarenoanthraquinones possess valuable spectral and photochemical properties. In particular, anthraoxazole derivatives **II** (X = N, Y = CH, Z = O) were proposed as reagents for fluorescent determination of spermatozoa [5]. Photochromic anthra[2,3-*d*]thiophenediones **II** (X = Y = CH, Z = S) have been patented as active medium for rewritable CDs [6], whereas hetarenoanthraquinones having α-alkoxy groups, e.g., 4,11-dimethoxynaphtho[2,3-*f*]indazole-5,10-diones **II** (X = CH, Y = N, Z = NH), exhibit fluorescence with a large Stokes shift [7]. Fluorophores with a large Stokes shift are promising as luminescent markers in biochemical studies, for their fluorescence is not quenched by biomolecules and such markers are detected as a rule in that spectral region where no fluorescence of biomolecules is observed [8].

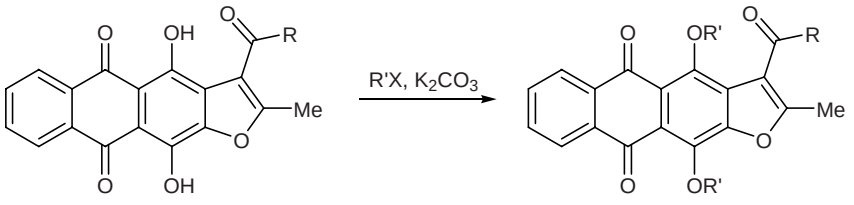


I, Z = S, Se, O.

While performing systematic studies on the synthesis and properties of linearly fused hetarenoanthraquinones, we prepared a series of alkoxy and amino derivatives of anthra[2,3-*b*]furan-5,10-dione **II** (X = Y = CH, Z = O) and examined their fluorescent properties. Up to now, only two methoxy derivatives of anthra[2,3-*b*]furan-5,10-dione were reported; however, their spectral parameters were not given [9, 10].

As starting compounds we used 3-substituted 4,11-dihydroxy-2-methylanthra[2,3-*b*]furan-5,10-diones **IIIa** and **IIIb** which were synthesized from quinizarin according to the procedure described in [11]. Alkylation of ester **IIIa** with dimethyl sulfate in acetone in the presence of potassium carbonate [12] gave the corresponding dimethoxy derivative **IVa** (Scheme 1). However, the yield of **IVa** was poor, presumably because of low solubility of both initial dihydroxyanthrafurandione **IIIa** and the salt derived therefrom. Higher yields of O-alkyl derivatives were obtained using the corresponding alkyl iodides as described in [9]. By alkylation of **IIIa** and **IIIb** with ethyl iodide or propyl iodide in DMF in the presence of potassium carbonate we synthesized dialkoxy derivatives **IVb**, **Va**, **VIa**. We found that the nature of the alkoxy groups in **IVa**–**VIa** weakly affects their spectral properties. Therefore, in the subsequent syntheses we

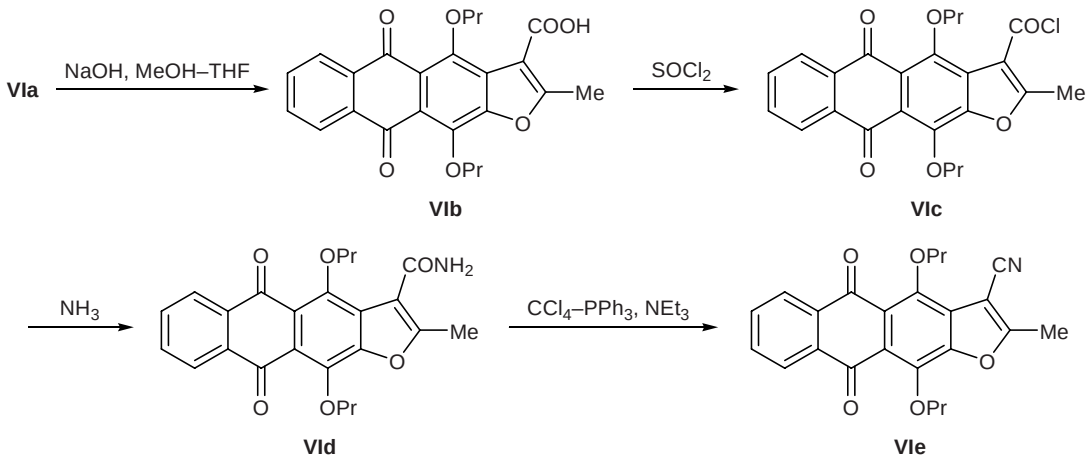
Scheme 1.



IIIa, **IIIb** **IVa**, **IVb**, **Va**, **VIa**

R′X = Me_2SO_4, EtI, PrI; **III**, R = OEt (**a**), Me (**b**); **IV**, R = OEt, R′ = Me (**a**); R = Me, R′ = Pr (**b**); **Va**, R = OEt, R′ = Et; **VIa**, R = OEt, R′ = Pr.

Scheme 2.



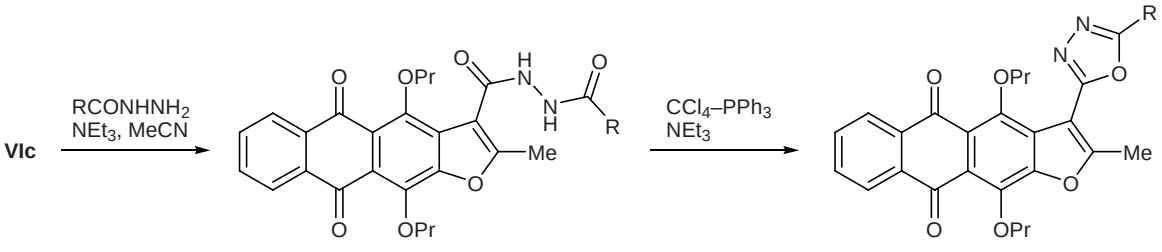
VIb **VIc** **VId** **VIe**

used propoxy derivatives that are better soluble in organic solvents and are formed in higher yields than their methoxy- or ethoxy-substituted analogs.

Hydrolysis of the ester group in **VIa** gave anthrafurandione-3-carboxylic acid **VIb** which was converted into the corresponding acid chloride **VIc** by treatment with thionyl chloride in toluene. Reaction of **VIc** with ammonia in methanol gave amide **VId**, and the latter was dehydrated according to the procedure described in [13] by the action of triphenylphosphine in carbon tetrachloride in the presence of triethylamine to obtain nitrile **VIe** (Scheme 2).

Taking into account that 2,5-diaryl-1,3,4-oxadiazoles are known to be effective fluorophores [14], we synthesized a series of 1,3,4-oxadiazole derivatives on the basis of acid **VIb**. By acylation of benzohydrazide with chloride **VIc** we obtained *N*,*N*′-diacylhydrazine **VIIa**. According to published data, cyclodehydration of *N*,*N*′-diacylhydrazides to oxadiazoles requires severe conditions (heating with $POCl_3$ or PCl_5), and their yields do not exceed 30–50% [15]. We found that *N*,*N*′-diacylhydrazine **VIIa** readily undergoes cyclodehydration under relatively mild conditions, by the action of CCl_4–PPh_3 in the presence of NEt_3, and that the target oxadiazole **VIIIa** is formed in a good yield.

Scheme 3.

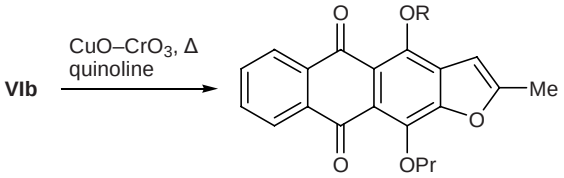


VIIa–**VIIf** **VIIIa**–**VIIIf**

R = Ph (**a**), CF_3 (**b**), 2-ClC_6H_4 (**c**), 2-HOC_6H_4 (**d**), 1,3-thiazol-2-yl (**e**), 4-$BocNHC_6H_4$ (**f**).

Following an analogous procedure, we synthesized a series of 3-(1,3,4-oxadiazol-2-yl)anthra[2,3-*b*]furan-5,10-dione derivatives **VIIIb**–**VIIIf**. Some intermediate *N*,*N*′-diacylhydrazines (compounds **VIIb** and **VIIf** were isolated as individual substances and characterized by spectral data. Modification of this procedure allowed us to obtain oxadiazoles **VIIIc**–**VIIIe** in a one-pot mode without isolation of intermediate *N*,*N*′-diacylhydrazides (Scheme 3). The synthesis of aminophenyl-substituted oxadiazole required preliminary protection of the amino group in initial *p*-aminobenzohydrazide; for this purpose, it was converted into the corresponding *N*-*tert*-butoxycarbonyl derivative, and the Boc protection turned out to be stable under mild cyclodehydration conditions. The subsequent deprotection of oxadiazole **VIIIf** by treatment with trifluoroacetic acid gave aminophenyloxadiazole **VIIIg**. Acid **VIb** was also subjected to decarboxylation [16] by heating in boiling quinoline in the presence of copper(II) chromite. As a result, we isolated 2-methylanthra[2,3-*b*]furan-5,10-dione (**IXa**) and by-product **IXb** formed by dealkylation of **IXa** (Scheme 4).

Scheme 4.



IXa, **IXb**

R = Pr (**a**), H (**b**).

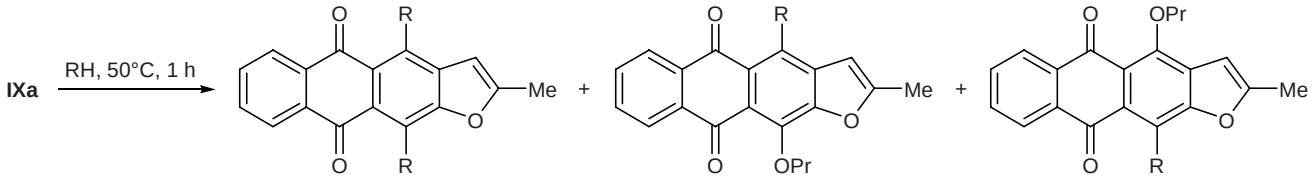
α-Alkoxy groups in anthraquinones and its hetero-ring-fused derivatives are activated to aromatic nucleophilic substitution due to effect of the quinone fragment, and they can be replaced by amino groups [17–19]. Dipropoxy-substituted anthrafurandione **IXa** readily reacted with primary and secondary amines to give the corresponding aminoanthra[2,3-*b*]furan-5,10-diones. Heating of **IXa** with 2-aminoethanol or pyrrolidine over a period of 1 h resulted in formation of a mixture of mono- and diamino derivatives. The major products were diamines **Xa** and **Xb**, while 4-amino derivatives **XIa** and **XIb** predominated among monosubstitution products (Scheme 5). These compounds were isolated by chromatography. Increase of the reaction time to 2 h leads to preferential formation of diamines **Xa** and **Xb (**yield 75–80%).

The structure of the isolated compounds was confirmed by spectral and analytical data. The structure of dealkylated compound **IXb** and monoamines **XIa**, **XIb**, and **XIIa** was proved by NMR spectroscopy. Compounds **XIa**, **XIb**, and **XIIa** showed nuclear Overhauser effect between 3-H and protons in the CH_2 group of the substituent on C^4, indicating spatially close arrangement of these protons. No analogous effect was observed for hydroxy derivative **IXb**; this means that the alkoxy group is attached to C^{11}.

As follows from the electronic absorption spectra of alkoxy-substituted anthra[2,3-*b*]furan-5,10-diones **IV**–**IX** and 1,4-dimethoxyanthraquinone (λ_{max} 428 nm [20]), fusion of a furan ring induces an appreciable blue shift of the absorption maxima (by 35–40 nm). In keeping with the color theory [21], these data suggest strong interaction between the fused furan ring and carbonyl groups, which leads to rupture of conjugation between the carbonyl and alkoxy groups.

All the obtained anthrafurandiones exhibit fluorescence in solution. In going from anthrafurandiones **IIIa** and **IIIb** to their *O*-alkyl derivatives, the Stokes shift strongly increases (see table). For example, it reaches 161 nm for dipropoxyanthrafurandione **VIa** against 79 nm for dihydroxy analog **IIIa**. Analogous Stokes shifts were found for the other 4,11-dialkoxy derivatives. The largest values (194–200 nm) are characteristic of acid **VIb**, *N*,*N*′-diacylhydrazine **VIIa**, and oxadiazole **VIIIb**. Our results also show that the nature of substituent in the 3-position only slightly affects the magnitude of the Stokes shift (within 30–40 nm); on the other hand, it can influence the fluorescence intensity of dipropoxy derivatives. Anthrafurandione **IXa** having no substituent on C^3 and oxadiazole derivatives

Scheme 5.



Xa, **Xb** **XIa**, **XIb** **XIIa**

R = $HOCH_2CH_2N$ (**a**), pyrrolidin-1-yl (**b**).

VIIIa, **VIIIb**, and **VIIIe** showed the maximal fluorescence intensity. The Stokes shift depends more strongly on the substituents in positions *4* and *11*. Hydrolysis of one propoxy group in compound **IXa** ($\Delta\lambda$ = 176 nm) is accompanied by decrease of the Stokes shift to 132 nm for **IXb**. Replacement of the propoxy groups by amino results in even more considerable reduction of the Stokes shift. Tertiary amines are characterized by lower $\Delta\lambda$ values as compared to secondary amines. Comparison of the spectral parameters of 4,11-dimethoxynaphtho[2,3-*f*]indazole-5,10-dione (**II**, X = CH, Y = N, Z = NH; $\Delta\lambda$ = 147 nm [7]) and 4,11-dipropoxyanthra[2,3-*b*]furan-5,10-dione (**IXa**) shows that replacement of fused pyrazole ring by furan increases the Stokes shift by 30 nm. Taking into account that intramolecular proton transfer in most of the synthesized alkoxyanthra[2,3-*b*]furan-5,10-diones is impossible, their large Stokes shifts are likely to result from considerable changes in the molecular geometry upon excitation.

The results of our study demonstrate prospects in further search for fluorophores with large Stokes shifts among the series of alkoxy derivatives of hetarenoanthraquinones.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz) using tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT SSQ 710 instrument with direct sample admission into the ion source (ion source temperature 150°C; samples were heated to 350°C). The electronic absorption spectra were measured on a Hitachi U-2000 spectrophotometer. The fluorescence spectra were recorded on Shimadzu RF-500 and Varian Cary Eclipce spectrofluorimeters. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 and Kiselgel F_{254} (Merck) plates. Kiselgel Merck 60 silica gel was used for preparative chromatography.

Ethyl 4,11-dimethoxy-2-methyl-5,10-dioxoanthra[2,3-*b*]furan-3-carboxylate (IVa). Powdered potassium carbonate, 2.0 g (14.5 mmol), was added to a suspension of 200 mg (0.55 mmol) of ester **IIIa** [11] in 50 ml of acetone, 1.0 ml (10.7 mmol) of freshly distilled dimethyl sulfate was then added, the mixture was heated at the boiling point under stirring for 12 h and filtered while hot, and the filtrate was cooled and acidified with 5% hydrochloric acid. The product was extracted into ethyl acetate, the extract was washed with water, dried, and evaporated, and the residue was subjected to chromatography on silica gel (eluent toluene–EtOAc, 9:1), followed by recrystallization from toluene. Yield 60 mg (28%), yellow crystals, mp 110–112°C. UV spectrum (EtOH), λ_{max}, nm (logε): 204 (4.3), 248 (4.4), 272 (4.5), 385 (3.8). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.46 t (3H, $OCH_2C\mathbf{H}_3$, J = 8.0 Hz), 2.75 s (3H, CH_3), 4.00 s (3H, OCH_3), 4.22 s (3H, OCH_3), 4.42–4.49 m (2H, $OC\mathbf{H}_2CH_3$), 7.71–7.76 m (2H, 7-H, 8-H), 8.18–8.24 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 394 (100) $[M]^+$, 366 (29) $[M - C_2H_4]^+$, 348 (80) $[M - OC_2H_5 - H]^+$, 335 (32) $[M - C_2H_4 - OCH_3]^+$, 321 (8) $[M - CO_2C_2H_5]^+$, 320 (33), 304 (5), 291 (10). Found, %: C 67.12; H 4.41. $C_{22}H_{18}O_7$. Calculated, %: C 67.00; H 4.60. M 394.11.

Long-wave absorption maxima in the electronic spectra and emission maxima in the fluorescence spectra of anthra[2,3-*b*]furan-5,10-dione derivatives in ethanol

Comp. no.	λ_{max}, nm		$\Delta\lambda$, nm
	absorption	fluorescence	
IIIa	505	575	70
IVa	381	560	179
IVb	388	566	178
Va	381	541	160
VIa	384	545	161
VIb	380	580	200
VId	385	575	190
VIIa	379	572	193
VIIIa	384	569	185
VIIIb	381	575	194
VIIIc	384	570	186
VIIId	383	571	188
VIIIe	385	560	175
VIIIg	384	567	183
IXa	392	568	176
IXb	439	571	132
Xa	595	621	26
Xb	557	571	14
XIb	507	571	64
XIIa	512	598	86

3-Acetyl-2-methyl-4,11-dipropoxyanthra[2,3-*b*]-furan-5,10-dione (IVb). Powdered potassium carbonate, 2.5 g (18 mmol), was added to a solution of 0.5 g (1.6 mmol) of ketone **IIIb** [11] in 30 ml of DMF, 2.5 ml (25.7 mmol) of propyl iodide was added, and

the mixture was stirred for 2 h at 95°C and cooled to room temperature. The precipitate was filtered off, the filtrate was acidified with 5% hydrochloric acid and extracted with ethyl acetate (2×100 ml), the extract was washed with water, dried, and evaporated, and the residue was purified by column chromatography on silica gel using toluene as eluent, followed by recrystallization from toluene. Yield 0.40 g (61%), yellow crystals, mp 157–159°C. UV spectrum (EtOH), λ_{max}, nm (logε): 208 (4.4), 246 (4.3), 260 (4.5), 388 (3.7). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.99 t (3H, CH_3, J = 7.5 Hz), 1.15 t (3H, CH_3, J = 7.5 Hz), 1.90 m (2H, CH_2), 2.02 m (2H, CH_2), 2.61 s (3H, CH_3), 2.72 s (3H, CH_3), 3.97 t (2H, OCH_2, J = 7.3 Hz), 4.33 t (2H, OCH_2, J = 6.8 Hz), 7.71–7.76 m (2H, 7-H, 8-H), 8.19–8.24 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 420 (35) $[M]^+$, 378 (10) $[M - C_3H_6]^+$, 363 (3), 349 (20), 337 (100), 321 (45), 43 (39). Found, %: C 71.33; H 5.64. $C_{25}H_{24}O_6$. Calculated, %: C 71.42; H 5.75. M 420.16.

Ethyl 2-methyl-4,11-diethoxy-5,10-dioxoanthra-[2,3-*b*]furan-3-carboxylate (Va). Ester **IIIa** [11], 0.8 g (2.2 mmol), was dissolved in 45 ml of DMF, 3.0 g (22 mmol) of powdered potassium carbonate and 3.0 ml (37.2 mmol) of ethyl iodide were added, and the mixture was stirred for 1 h at 100°C and cooled to room temperature. The precipitate was filtered off, the filtrate was acidified with 5% hydrochloric acid and extracted with ethyl acetate, the extract was washed with water, dried, and evaporated, and the residue was purified by column chromatography on silica gel using toluene as eluent. Yield 0.48 g (52%), yellow crystals, mp 121–122°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40–1.61 m (9H, CH_3), 2.71 s (3H, CH_3), 4.09–4.20 m (2H, CH_2), 4.36–4.50 m (4H, CH_2), 7.68–7.73 m (2H, 7-H, 8-H), 8.17–8.22 m (2H, 6-H, 9-H). Found, %: C 68.33; H 5.34. $C_{24}H_{22}O_7$. Calculated, %: C 68.24; H 5.25.

Ethyl 2-methyl-4,11-dipropoxy-5,10-dioxoanthra[2,3-*b*]furan-3-carboxylate (VIa). Powdered potassium carbonate, 1.5 g (10.9 mmol), was added to a solution of 0.5 g (1.5 mmol) of ester **IIIa** [11] in 25 ml of DMF, 1.5 ml (15.4 mmol) of propyl iodide was added, and the mixture was stirred for 1.5 h at 100–110°C and cooled to room temperature. The precipitate was filtered off, the filtrate was acidified with 5% hydrochloric acid and extracted with ethyl acetate (2×100 ml), the extract was washed with water, dried, and evaporated, and the residue was recrystallized from toluene. Yield 0.45 g (66%), yellow crystals, mp 129–130°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 t (3H, CH_3, J = 7.0 Hz), 1.13 t (3H, CH_3, J = 7.9 Hz), 1.42 t (3H, CH_3, J = 7.0 Hz), 1.89–2.04 m (4H, CH_2), 2.70 s (3H, CH_3), 4.00 t (2H, OCH_2, J = 7.0 Hz), 4.30 t (2H, OCH_2, J = 6.0 Hz), 4.38–4.49 m (2H, CH_2), 7.69–7.75 m (2H, 7-H, 8-H), 8.17–8.22 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 450 (17) $[M]^+$, 421 (13) $[M - C_2H_5]^+$, 405 (18) $[M - OC_2H_5]^+$, 366 (61) $[M - C_3H_6]^+$, 320 (100), 292 (6). Found, %: C 69.45; H 5.65. $C_{26}H_{26}O_7$. Calculated, %: C 69.32; H 5.82. M 450.17.

2-Methyl-5,10-dioxo-4,11-dipropoxyanthra-[2,3-*b*]furan-3-carboxylic acid (VIb). A solution of 1.0 g (25 mmol) of sodium hydroxide in a mixture of 30 ml of methanol and 20 ml of water was added to a solution of 1.3 g (2.9 mmol) of ester **VIa** in 30 ml of THF, and the mixture was stirred for 1.5 h at 40–50°C. It was then poured into water, neutralized with 5% hydrochloric acid, and extracted with ethyl acetate (2×100 ml). The extract was washed with water, dried, and evaporated, and the residue was recrystallized from toluene–petroleum ether, 1:4. Yield 0.88 g (72%), yellow crystals, mp 171–173°C. UV spectrum (EtOH), λ_{max}, nm (logε): 210 (4.4), 248 (4.3), 259 (4.5), 380 (3.8). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.02 t (3H, CH_3, J = 7.5 Hz), 1.13 t (3H, CH_3, J = 7.4 Hz), 1.96–2.11 m (4H, CH_2), 2.92 s (3H, CH_3), 4.20 t (2H, OCH_2, J = 7.4 Hz), 4.35 t (2H, OCH_2, J = 6.7 Hz), 7.74–7.78 m (2H, 7-H, 8-H), 8.21 m (2H, 6-H, 9-H), 12.08 br.s (1H, CO_2H). Mass spectrum, m/z (I_{rel}, %): 422 (21) $[M]^+$, 380 (11) $[M - C_3H_6]^+$, 378 (17) $[M - CO_2]^+$, 338 (35) $[M - 2C_3H_6]^+$, 320 (100) $[M - 2C_3H_6 - H_2O]^+$, 294 (59) $[M - 2C_3H_6 - CO_2]^+$, 43 (37) $[C_3H_7]^+$. Found, %: C 68.54; H 5.35. $C_{24}H_{22}O_7$. Calculated, %: C 68.24; H 5.25. M 422.14.

2-Methyl-5,10-dioxo-4,11-dipropoxyanthra-[2,3-*b*]furan-3-carbonyl chloride (VIc). Acid **VIb**, 100 mg (0.22 mmol), was dissolved in 3 ml of toluene, 0.1 ml (1.4 mmol) of thionyl chloride was added, and the mixture was heated for 15 min under reflux and evaporated. Yield 100 mg (96%), yellow oily substance which then crystallized, mp 84–87°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.04 t (3H, CH_3, J = 7.5 Hz), 1.12 t (3H, CH_3, J = 7.4 Hz), 1.92–2.03 m (4H, CH_2), 2.82 s (3H, CH_3), 4.00 t (2H, OCH_2, J = 7.0 Hz), 4.31 t (2H, OCH_2, J = 6.7 Hz), 7.73–7.77 m (2H, 7-H, 8-H), 8.16–8.20 m (2H, 6-H, 9-H).

2-Methyl-5,10-dioxo-4,11-dipropoxyanthra-[2,3-*b*]furan-3-carboxamide (VId). Acid chloride **VIc**, 100 mg (0.23 mmol), was dissolved in chloro-

form, 1 ml (12.2 mmol) of 23% aqueous ammonia was added, and the mixture was stirred for 20 min at room temperature and evaporated. The residue was dispersed in water and treated with ethyl acetate, the extract was washed with a solution of sodium carbonate and water, dried, and evaporated, and the product was recrystallized from toluene–petroleum ether (1:1). Yield 71 mg (73%), yellow crystals, mp 231–232°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.00 t (3H, CH_3, J = 7.5 Hz), 1.15 t (3H, CH_3, J = 7.4 Hz), 1.95–2.05 m (4H, CH_2), 2.88 s (3H, CH_3), 4.06 t (2H, OCH_2), 4.32 t (2H, OCH_2), 5.82 s (1H, $CONH_2$), 7.73–7.77 m (2H, 7-H, 8-H), 8.19–8.23 m (2H, 6-H, 9-H), 8.29 s (1H, $CONH_2$). Mass spectrum, m/z (I_{rel}, %): 421 (27) $[M]^+$, 404 (5) $[M - NH_3]^+$, 379 (8) $[M - C_3H_6]^+$, 362 (13) $[M - OC_3H_7]^+$, 337 (20) $[M - 2C_3H_6]^+$, 320 (100), 208 (10), 43 (79) $[C_3H_7]^+$. Found, %: C 68.25; H 5.34; N 3.39. $C_{24}H_{23}NO_6$. Calculated, %: C 68.40; H 5.50; N 3.32. *M* 421.15.

2-Methyl-5,10-dioxo-4,11-dipropoxyanthra[2,3-*b*]furan-3-carbonitrile (VIe). Amide **VId**, 50 mg (0.12 mmol), was heated in boiling acetonitrile until complete dissolution. The solution was cooled to room temperature, and 0.1 ml (0.72 mmol) of triethylamine, 1.0 ml (10.4 mmol) of carbon tetrachloride, and 50 mg (0.19 mmol) of triphenylphosphine were added under stirring. The mixture was stirred for 30 min and diluted with an equal volume of petroleum ether, the precipitate of triphenylphosphine oxide was filtered off, ethyl acetate was added to the filtrate, the solution was washed with 5% hydrochloric acid and water, dried, and evaporated, and the residue was purified by column chromatography on silica gel (eluent toluene–petroleum ether, 1:1), followed by recrystallization from toluene. Yield 35 mg (73%), yellow crystals, mp 175–176°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 t (3H, CH_3, J = 7.5 Hz), 1.14 t (3H, CH_3, J = 7.5 Hz), 1.94–2.03 m (2H, CH_2), 2.05–2.14 m (2H, CH_2), 2.76 s (3H, CH_3), 4.14 t (2H, OCH_2, J = 7.3 Hz), 4.33 t (2H, OCH_2, J = 6.8 Hz), 7.72–7.77 m (2H, 7-H, 8-H), 8.18–8.23 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 403 (8) $[M]^+$, 361 (9) $[M - C_3H_6]^+$, 320 (100), 318 (10), 43 (32) $[C_3H_7]^+$. Found, %: C 71.34; H 5.33; N 3.41. $C_{24}H_{21}NO_5$. Calculated, %: C 71.45; H 5.25; N 3.47. *M* 403.14.

***N′*-Benzoyl-2-methyl-5,10-dioxo-4,11-dipropoxyanthra[2,3-*b*]furan-3-carbohydrazide (VIIa).** A solution of 68 mg (0.5 mmol) of benzohydrazide in 5 ml of acetonitrile and 0.1 ml (0.72 mmol) of triethylamine were added to a solution of 100 mg (0.23 mmol) of acid chloride **VIc** in chloroform. The mixture was stirred for 30 min, evaporated, and treated with water, and the precipitate was filtered off, dried in air, and recrystallized from toluene. Yield 104 mg (77%), yellow crystals, mp 208–210°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.93 t (3H, CH_3, J = 7.5 Hz), 1.15 t (3H, CH_3, J = 7.4 Hz), 1.90–2.05 m (4H, CH_2), 2.90 s (3H, CH_3), 4.22 t (2H, OCH_2, J = 7.4 Hz), 4.31 t (2H, OCH_2, J = 6.8 Hz), 7.46–7.50 m (2H, C_6H_5), 7.55–7.59 m (1H, C_6H_5), 7.73–7.77 m (2H, 7-H, 8-H), 7.89–7.92 m (2H, C_6H_5), 8.20–8.24 m (2H, 6-H, 9-H), 8.93 d (1H, NH, J = 4.4 Hz), 11.16 d (1H, NH, J = 4.4 Hz). Mass spectrum, m/z (I_{rel}, %): 540 (14) $[M]^+$, 498 (9) $[M - C_3H_6]^+$, 405 (5) $[M - PhCONHNH]^+$, 363 (52) $[M - C_3H_6 - PhCONHNH]^+$, 321 (64) $[M - 2C_3H_6 - PhCONHNH]^+$, 105 (79) $[C_6H_5CO]^+$, 43 (100) $[C_3H_7]^+$. Found, %: C 68.95; H 5.16; N 5.16. $C_{31}H_{28}N_2O_7$. Calculated, %: C 68.88; H 5.22; N 5.18. *M* 540.19.

2-Methyl-5,10-dioxo-4,11-dipropoxy-*N′*-(trifluoroacetyl)anthra[2,3-*b*]furan-3-carbohydrazide (VIIb) was synthesized in a similar way from compound **VIc** and trifluoroacetohydrazide. Yield 84%, yellow crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.93 t (3H, CH_3, J = 7.5 Hz), 1.18 t (3H, CH_3, J = 7.5 Hz), 1.85–1.94 m (2H, CH_2), 1.97–2.07 m (2H, CH_2), 2.88 s (3H, CH_3), 4.20 t (2H, OCH_2, J = 7.4 Hz), 4.33 t (2H, OCH_2, J = 6.8 Hz), 7.77–7.81 m (2H, 7-H, 8-H), 8.22–8.25 m (2H, 6-H, 9-H), 9.27 d (1H, NH, J = 4.5 Hz), 11.21 d (1H, NH, J = 4.5 Hz). Found, %: C 58.46; H 4.44; N 5.19. $C_{26}H_{23}F_3N_2O_7$. Calculated, %: C 58.65; H 4.35; N 5.26.

***N′*-[4-(*tert*-Butoxycarbonylamino)benzoyl]-2-methyl-5,10-dioxo-4,11-dipropoxyanthra[2,3-*b*]-furan-3-carbohydrazide (VIIf)** was synthesized in a similar way from chloride **VIc** and 4-(*tert*-butoxycarbonylamino)benzohydrazide. Yield 68%, yellow crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84–1.00 m (6H, CH_3), 1.56 s [9H, $C(CH_3)_3$], 1.93–2.05 m (4H, CH_2), 2.91 s (3H, CH_3), 4.25 t (2H, OCH_2, J = 7.5 Hz), 4.34 t (2H, OCH_2, J = 6.7 Hz), 6.75 s (1H, NH), 7.50 d (2H, C_6H_4, J = 8.6 Hz), 7.73–7.77 m (2H, 7-H, 8-H), 7.86 d (2H, C_6H_4, J = 8.5 Hz), 8.22–8.26 m (2H, 6-H, 9-H), 8.82 d (1H, NH, J = 4.9 Hz), 11.05 d (1H, NH, J = 4.9 Hz). Found, %: C 65.90; H 5.46; N 6.40. $C_{36}H_{37}N_3O_9$. Calculated, %: C 65.94; H 5.69; N 6.41.

2-Methyl-3-(5-phenyl-1,3,4-oxadiazol-2-yl)-4,11-dipropoxyanthra[2,3-*b*]furan-5,10-dione (VIIIa). Diacylhydrazine **VIIa**, 60 mg, was dissolved on heating in a 1:3 chloroform–acetonitrile mixture, 0.2 ml (1.44 mmol) of triethylamine and 1.0 ml (10.4 mmol)

of carbon tetrachloride were added, and 100 mg (0.38 mmol) of triphenylphosphine was then added in portions until the initial hydrazide disappeared (according to the TLC data). The mixture was stirred for 30 min and diluted with an equal volume of petroleum ether, the precipitate of triphenylphosphine oxide was filtered off, the filtrate was treated with ethyl acetate, the extract was washed with 5% hydrochloric acid and a solution of sodium carbonate, the solvent was distilled off under reduced pressure, and the residue was purified by column chromatography on silica gel using toluene as eluent, followed by recrystallization from toluene. Yield 41 mg (70%), yellow crystals, mp 179–180°C. UV spectrum (EtOH), λ_{max}, nm (logε): 202 (4.3), 244 (4.3), 258 (4.5), 386 (3.8). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.72 t (3H, CH_3, J = 7.4 Hz), 1.17 t (3H, CH_3, J = 7.5 Hz), 1.48–1.57 m (2H, CH_2), 1.99–2.08 m (2H, CH_2), 2.80 s (3H, CH_3), 3.87 t (2H, OCH_2, J = 7.2 Hz), 4.39 t (2H, OCH_2, J = 6.8 Hz), 7.53–7.57 m (1H, C_6H_5), 7.59–7.62 m (2H, 7-H, 8-H), 7.73–7.76 m (2H, C_6H_5), 8.17–8.20 m (2H, C_6H_5), 8.21–8.24 m (2H, 6-H, 9-H). Mass spectrum, *m*/*z* (I_{rel}, %): 522 (55) $[M]^+$, 480 (17) $[M - C_3H_6]^+$, 438 (100) $[M - 2C_3H_6]^+$, 321 (20), 105 (33) $[C_6H_5CO]^+$, 43 (33) $[C_3H_7]^+$. Found, %: C 71.37; H 4.92; N 5.22. $C_{31}H_{26}N_2O_6$. Calculated, %: C 71.25; H 5.02; N 5.36. *M* 522.18.

2-Methyl-4,11-dipropoxy-3-(5-trifluoromethyl)-1,3,4-oxadiazol-2-yl)anthra[2,3-*b*]furan-5,10-dione (VIIIb) was synthesized in a similar way from diacylhydrazine **VIIb**. Yield 81%, yellow crystals, mp 161–162°C. UV spectrum (EtOH), λ_{max}, nm (logε): 202 (4.3), 244 (4.2), 260 (4.5), 382 (3.7). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (3H, CH_3, J = 7.5 Hz), 1.16 t (3H, CH_3, J = 7.5 Hz), 1.61–1.69 m (2H, CH_2), 1.98–2.06 m (2H, CH_2), 2.81 s (3H, CH_3), 3.90 t (2H, OCH_2, J = 7.4 Hz), 4.36 t (2H, OCH_2, J = 6.8 Hz), 7.73–7.77 m (2H, 7-H, 8-H), 8.19–8.23 m (2H, 6-H, 9-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 182.64 (C=O), 182.53 (C=O), 163.90, 161.24, 155.96 q (**C**CF_3, J = 44.6 Hz); 150.46, 149.97, 142.44, 134.24, 134.12, 126.49, 123.68 122.54; 116.15 q (CF_3, J = 272.1 Hz), 101.74, 133.51 (CH), 133.43 (CH), 126.58 (CH), 126.42 (CH), 77.98 (CH_2), 77.10 (CH_2), 23.39 (CH_2), 22.77 (CH_2), 14.05 (CH_3), 10.21 (CH_3), 9.57 (CH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 514 (10) $[M]^+$, 472 (9) $[M - C_3H_6]^+$, 445 (1) $[M - CF_3]^+$, 430 (100) $[M - 2C_3H_6]^+$, 321 (6), 69 (5), 43 (39) $[C_3H_7]^+$. Found, %: C 60.66; H 4.32; N 5.61. $C_{26}H_{21}F_3N_2O_6$. Calculated, %: C 60.70; H 4.11; N 5.45. *M* 514.14.

3-[5-(2-Chlorophenyl)-1,3,4-oxadiazol-2-yl]-2-methyl-4,11-dipropoxyanthra[2,3-*b*]furan-5,10-dione (VIIIc). Acid chloride **VIc**, 100 mg (0.23 mmol), was dissolved in acetonitrile, 55 mg (0.33 mmol) of *o*-chlorobenzohydrazide and 0.5 ml (3.6 mmol) of triethylamine were added, the mixture was stirred for 30 min, 1 ml (10.4 mmol) of carbon tetrachloride was added, and 100 mg (0.38 mmol) of triphenylphosphine was then added in portions over a period of 30 min. When the reaction was complete (TLC), the mixture was treated as described above for the synthesis of compound **VIIIa**. Yield 91 mg (60%), yellow crystals, mp 124–125°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.73 t (3H, CH_3, J = 7.5 Hz), 1.16 t (3H, CH_3, J = 7.5 Hz), 1.49–1.58 m (2H, CH_2), 1.59–2.08 m (2H, CH_2), 2.81 s (3H, CH_3), 3.89 t (2H, OCH_2, J = 7.3 Hz), 4.38 t (2H, OCH_2, J = 6.8 Hz), 7.44–7.54 m (4H, C_6H_4Cl), 7.71–7.76 m (2H, 7-H, 8-H), 8.19–8.23 m (2H, 6-H, 9-H). Mass spectrum, *m*/*z* (I_{rel}, %): 556 (46) $[M]^+$, 514 (8) $[M - C_3H_6]^+$, 471 (10), 335 (6), 139 (48) $[C_6H_4ClCO]^+$, 43 (100) $[C_3H_7]^+$. Found, %: C 66.76; H 4.43; N 5.12. $C_{31}H_{25}ClN_2O_6$. Calculated, %: C 66.85; H 4.52; N 5.03. *M* 556.14.

3-[5-(2-Hydroxyphenyl)-1,3,4-oxadiazol-2-yl]-2-methyl-4,11-dipropoxyanthra[2,3-*b*]furan-5,10-dione (VIIId) was synthesized as described above for compound **VIIIc** from chloride **VIc** and 2-hydroxybenzohydrazide. Yield 45%, yellow crystals, mp 101–102°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.74 t (3H, CH_3, J = 7.4 Hz), 1.17 t (3H, CH_3, J = 7.5 Hz), 1.49–1.59 m (2H, CH_2), 2.00–2.09 m (2H, CH_2), 2.82 s (3H, CH_3), 3.78 t (2H, OCH_2, J = 7.2 Hz), 4.39 t (2H, OCH_2, J = 6.8 Hz), 7.03–7.06 m (1H, C_6H_4), 7.19 m (1H, C_6H_4), 7.48–7.52 m (1H, C_6H_4), 7.73–7.77 m (2H, 7-H, 8-H), 7.90 m (1H, C_6H_4), 8.20–8.25 m (2H, 6-H, 9-H), 10.13 s (1H, OH). Mass spectrum, *m*/*z* (I_{rel}, %): 538 (68) $[M]^+$, 496 (19) $[M - C_3H_6]^+$, 454 (100) $[M - 2C_3H_6]^+$, 321 (21), 319 (23), 121 (23) $[C_6H_4(OH)CO]^+$, 43 (72) $[C_3H_7]^+$. Found, %: C 69.32; H 4.96; N 5.12. $C_{31}H_{26}N_2O_7$. Calculated, %: C 69.14; H 4.86; N 5.20. *M* 538.17.

2-Methyl-4,11-dipropoxy-3-[5-(1,3-thiazol-2-yl)-1,3,4-oxadiazol-2-yl]anthra[2,3-*b*]furan-5,10-dione (VIIIe) was synthesized as described above for compound **VIIIc** from chloride **VIc** and 1,3-thiazole-2-carbohydrazide. Yield 76%, yellow crystals, mp 215–217°C. UV spectrum (EtOH), λ_{max}, nm (logε): 202 (4.3), 243 (4.3), 255 (4.5), (300), 385 (3.6). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.78 t (3H, CH_3, J = 7.4 Hz), 1.16 t (3H, CH_3, J = 7.5 Hz), 1.61–1.70 m (2H, CH_2), 1.98–2.07 m (2H, CH_2), 2.79 s (3H, CH_3),

3.95 t (2H, OCH_2, J = 7.2 Hz), 4.37 t (2H, OCH_2, J = 6.8 Hz), 6.99 d (1H, CH, J = 3.1 Hz), 7.71–7.76 m (2H, 7-H, 8-H), 8.10 d (1H, CH, J = 3.1 Hz), 8.18–8.23 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 529 (15) $[M]^+$, 487 (5) $[M - C_3H_6]^+$, 445 (67) $[M - 2C_3H_6]^+$, 362 (2), 321 (22) $[M - 2C_3H_6 - C_5H_2N_3OS]^+$, 320 (11), 43 (100) $[C_3H_7]^+$, 42 (30) $[C_3H_6]^+$. Found, %: C 63.47; H 4.26; N 7.82. $C_{28}H_{23}N_3O_6S$. Calculated, %: C 63.50; H 4.38; N 7.93. M 529.13.

3-{5-[4-(*tert*-Butoxycarbonylamino)phenyl]-1,3,4-oxadiazol-2-yl}-2-methyl-4,11-dipropoxyanthra[2,3-*b*]furan-5,10-dione (VIIIf) was synthesized as described above for compound **VIIIa** from diacylhydrazine **VIIf**. Yield 81%, yellow crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.72 t (3H, CH_3, J = 7.5 Hz), 1.16 t (3H, CH_3, J = 7.4 Hz), 1.55 s [9H, $C(CH_3)_3$], 1.60–1.70 m (2H, CH_2), 1.99–2.08 m (2H, CH_2), 2.78 s (3H, CH_3), 3.85 t (2H, OCH_2, J = 7.2 Hz), 4.38 t (2H, OCH_2, J = 6.8 Hz), 6.79 s (1H, NH), 7.56 d (2H, C_6H_4, J = 8.5 Hz), 7.72–7.76 m (2H, 7-H, 8-H), 8.10 d (2H, C_6H_4, J = 8.5 Hz), 8.19–8.24 m (2H, 6-H, 9-H). Found, %: C 67.71; H 5.43; N 6.71. $C_{36}H_{35}N_3O_8$. Calculated, %: C 67.81; H 5.53; N 6.59.

3-[5-(4-Aminophenyl)-1,3,4-oxadiazol-2-yl]-2-methyl-4,11-dipropoxyanthra[2,3-*b*]furan-5,10-dione (VIIIg). Compound **VIIIf**, 70 mg (0.1 mmol), was dissolved in 10 ml of methylene chloride, 0.5 ml (6.5 mmol) of trifluoroacetic acid was added, the mixture was stirred for 1 h, washed with water and a solution of sodium carbonate, dried, and evaporated, and the residue was recrystallized from toluene–petroleum ether (1:3). Yield 45 mg (80%), yellow crystals, mp 125–126°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.74 t (3H, CH_3, J = 7.4 Hz), 1.17 t (3H, CH_3, J = 7.4 Hz), 1.50–1.60 m (2H, CH_2), 2.00–2.08 m (2H, CH_2), 2.79 s (3H, CH_3), 3.59 t (2H, OCH_2, J = 7.3 Hz), 4.14 br.s (2H, NH_2), 4.39 t (2H, OCH_2, J = 6.8 Hz), 6.78 d (2H, C_6H_4, J = 8.6 Hz), 7.72–7.77 m (2H, 7-H, 8-H), 7.97 d (2H, C_6H_4, J = 8.6 Hz), 8.20–8.25 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 537 (97) $[M]^+$, 495 (15) $[M - C_3H_6]^+$, 452 (24) $[M - C_3H_6 - C_3H_7]^+$, 335 (3), 321 (11), 120 (60) $[C_6H_4(NH_2)CO]^+$, 92 (12) $[C_6H_4NH_2]^+$, 43 (100) $[C_3H_7]^+$, 42 (25) $[C_3H_6]^+$. Found, %: C 69.05; H 5.12; N 7.67. $C_{31}H_{27}N_3O_6$. Calculated, %: C 69.26; H 5.06; N 7.82. M 537.19.

2-Methyl-4,11-dipropoxyanthra[2,3-*b*]furan-5,10-dione (IXa) and 4-hydroxy-2-methyl-11-propoxyanthra[2,3-*b*]furan-5,10-dione (IXb). Acid **VIb**, 0.39 g (0.92 mmol), was dissolved in 3.0 ml of quinoline, 0.39 g (1.7 mmol) of copper(II) chromite was added, and the mixture was stirred for 30 min at the boiling point. The mixture was then poured into water, neutralized with 5% hydrochloric acid, and treated with ethyl acetate (2×70 ml), the extract was washed with water, dried, and evaporated, and the residue (a mixture of compounds **IXa** and **IXb**) was separated by column chromatography on silica gel using toluene–petroleum ether (9:1); the products were additionally recrystallized from toluene.

Compound **IXa**. Yield 0.18 g (51%), orange crystals, mp 163–164°C, R_f 0.66 (toluene–EtOAc, 10 : 1). UV spectrum (EtOH), λ_{max}, nm (log ε): 201 (4.3), 245 (4.5), 261 (4.4), 393 (3.9). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.07–1.13 m (6H, CH_3), 1.89–2.02 m (4H, CH_2), 2.52 d (3H, CH_3, J = 1.1 Hz), 4.12 t (2H, OCH_2, J = 6.7 Hz), 4.33 t (2H, OCH_2, J = 6.8 Hz), 6.62 q (1H, 3-H, J = 1.1 Hz), 7.65–7.70 m (2H, 7-H, 8-H), 8.15–8.20 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 378 (20) $[M]^+$, 338 (7) $[M - C_3H_6]^+$, 294 (42) $[M - 2C_3H_6]^+$, 44 (100), 43 (86) $[C_3H_7]^+$. Found, %: C 73.14; H 5.78. $C_{23}H_{22}O_5$. Calculated, %: C 73.00; H 5.86. M 378.15.

Compound **IXb**. Yield 31 mg (10%), orange crystals, mp 174–175°C, R_f 0.72 (toluene–EtOAc, 10 : 1). UV spectrum (EtOH), λ_{max}, nm (log ε): 201 (4.4), 250 (4.5), 262 (4.4), 442 (4.0). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.14 t (3H, CH_3, J = 7.4 Hz), 1.95–2.04 m (2H, CH_2), 2.56 d (3H, CH_3, J = 1.0 Hz), 4.31 t (2H, OCH_2, J = 6.8 Hz), 6.73 q (1H, 3-H, J = 1.0 Hz), 7.73–7.80 m (2H, 7-H, 8-H), 8.29–8.33 m (2H, 6-H, 9-H), 14.24 s (1H, OH). Found, %: C 71.57; H 4.62. $C_{20}H_{16}O_5$. Calculated, %: C 71.42; H 4.79.

4,11-Bis[(2-hydroxyethyl)amino]-2-methylanthra[2,3-*b*]furan-5,10-dione (Xa), 4-[(2-hydroxyethyl)amino]-2-methyl-11-propoxyanthra[2,3-*b*]-furan-5,10-dione (XIa), and 11-[(2-hydroxyethyl)-amino]-2-methyl-4-propoxyanthra[2,3-*b*]furan-5,10-dione (XIIa). 2-Aminoethanol, 3.0 ml (50 mmol), was added to 200 mg (0.53 mmol) of anthrafurandione **IXa**, and the mixture was stirred for 1 h at 50°C, poured into water, and extracted with ethyl acetate. The extract was washed with water, dried, and evaporated, and the residue was subjected to column chromatography on silica gel using chloroform–methanol (1:0 to 2:1) as eluent.

Compound **Xa**. Yield 44%, dark blue crystals, mp 262–264°C, R_f 0.1 (toluene–ethyl acetate, 5:3). UV spectrum (EtOH), λ_{max}, nm (log ε): 202 (4.3), 235 (4.2), 261 (4.6), 344 (3.7), (482), 523 (3.8), 555 (4.3), 598 (4.4). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.47 d (3H, CH_3), 3.70 m (2H, CH_2), 3.91–3.99 m (4H, CH_2),

3.95 m (2H, CH_2), 4.98 t (1H, OH, J = 5.0 Hz), 5.09 t (1H, OH, J = 5.1 Hz), 7.09 s (1H, 3-H), 7.72–7.77 m (2H, 7-H, 8-H), 8.22–8.27 m (2H, 6-H, 9-H), 11.88 t (1H, NH, J = 5.4 Hz), 12.40 t (1H, NH, J = 4.7 Hz). Mass spectrum, m/z (I_{rel}, %): 380 (93) $[M]^+$, 363 (3) $[M - OH]^+$, 349 (100) $[M - CH_2OH]^+$, 320 (9) $[M - NHCH_2CH_2OH]^+$, 318 (34) $[M - 2CH_2OH]^+$, 304 (11), 290 (20) $[M - 2CH_2CH_2OH]^+$, 289 (16), 275 (7). Found, %: C 66.24; H 5.26; N 7.50. $C_{21}H_{20}N_2O_5$. Calculated, %: C 66.31; H 5.30; N 7.36. M 380.14.

Compound **XIa**. Yield 28%, red–brown crystals, mp 192–193°C, R_f 0.38 (toluene–ethyl acetate, 5:3). UV spectrum (EtOH), λ_{max}, nm (log ε): 204 (4.1), 260 (4.5), 325 (3.5), 518 (3.9), (555). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.12 t (3H, CH_3, J = 7.5 Hz), 1.92–2.03 m (2H, CH_2), 2.50 s (3H, CH_3), 3.83 t (2H, CH_2OH, J = 5.2 Hz), 4.05 t (2H, NHC**H**$_2$, J = 5.4 Hz), 4.20 t (2H, OCH_2, J = 6.8 Hz), 6.81 d (1H, 3-H, J = 0.8 Hz), 7.64–7.69 m (2H, 7-H, 8-H), 8.18–8.22 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 379 (51) $[M]^+$, 348 (26) $[M - CH_2OH]^+$, 337 (11) $[M - C_3H_6]^+$, 336 (16) $[M - C_3H_7]^+$, 319 (7) $[M - NHCH_2CH_2OH]^+$, 306 (100) $[M - C_3H_6 - CH_2OH]^+$, 304 (9), 43 (61) $[C_3H_7]^+$, 42 (15) $[C_3H_6]^+$. Found, %: C 69.84; H 5.76; N 3.54. $C_{22}H_{21}NO_5$. Calculated, %: C 69.65; H 5.58; N 3.69. M 379.14.

Compound **XIIa**. Yield 5%, red–brown crystals, mp 165–166°C, R_f 0.55 (toluene–ethyl acetate, 5:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 t (3H, CH_3, J = 7.5 Hz), 1.88–2.01 m (2H, CH_2), 2.53 d (3H, CH_3, J = 1.0 Hz), 3.98–4.12 m (6H, CH_2), 6.62 s (1H, 3-H), 7.66–7.71 m (2H, 7-H, 8-H), 8.21–8.24 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 379 (49) $[M]^+$, 348 (24) $[M - CH_2OH]^+$, 337 (9) $[M - C_3H_6]^+$, 336 (33) $[M - C_3H_7]^+$, 320 (6) $[M - OC_3H_7]^+$, 319 (9) $[M - NHCH_2CH_2OH]^+$, 306 (100) $[M - C_3H_6 - CH_2OH]^+$, 304 (11) $[M - NHCH_2CH_2OH - CH_3]^+$, 292 (8) $[M - C_3H_6 - CH_2CH_2OH]^+$, 277 (5) $[M - NHCH_2CH_2OH - C_3H_6]^+$, 43 (61) $[C_3H_7]^+$. Found, %: C 69.71; H 5.45; N 3.65. $C_{22}H_{21}NO_5$. Calculated, %: C 69.65; H 5.58; N 3.69. M 379.14.

2-Methyl-4,11-bis(pyrrolidin-1-yl)anthra[2,3-*b*]-furan-5,10-dione (Xb) and 2-methyl-11-propoxy-4-(pyrrolidin-1-yl)anthra[2,3-*b*]furan-5,10-dione (XIb). A mixture of 200 mg (0.53 mmol) of compound **IXa** and 3 ml (36 mmol) of pyrrolidine was heated for 1 h at 50–60°C. The mixture was then poured into water and extracted with ethyl acetate, the extract was washed with water, dried, and evaporated, and the residue was separated by column chromatography in silica gel using toluene–ethyl acetate (1:0 to 2:1) as eluent.

Compound **Xb**. Yield 52%, dark blue crystals, mp 160–161°C, R_f 0.38 (toluene–ethyl acetate, 5:2). UV spectrum (EtOH), λ_{max}, nm (log ε): 204 (4.4), 275 (4.6), 365 (3.8), 404 (3.7), (520), 567 (4.1), (600). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.97–2.05 m (8H, CH_2), 2.47 s (3H, CH_3), 3.46–3.62 m (8H, CH_2), 6.79 s (1H, 3-H), 7.59–7.63 m (2H, 7-H, 8-H), 8.15–8.18 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 398 (100) $[M - 2H]^+$, 383 (25), 342 (14), 330 (52) $[M - C_4H_8N]^+$, 288 (10), 70 (18) $[C_4H_8N]^+$. Found, %: C 74.87; H 6.12; N 7.08. $C_{25}H_{24}N_2O_3$. Calculated, %: C 74.98; H 6.04; N 7.00. M 400.18.

Compound **XIb**. Yield 30%, red–brown crystals, mp 195–196°C, R_f 0.64 (toluene–ethyl acetate, 5:2). UV spectrum (EtOH), λ_{max}, nm (log ε): 204 (4.4), 261 (4.5), 344 (3.6), (360), 507 (3.8). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 t (3H, CH_3, J = 7.3 Hz), 1.93–2.06 m (6H, CH_2), 2.50 s (3H, CH_3), 3.52 t (4H, CH_2, J = 6.3 Hz), 4.18 t (2H, OCH_2, J = 6.9 Hz), 6.80 d (1H, 3-H, J = 0.9 Hz), 7.62–7.68 m (2H, 7-H, 8-H), 8.16–8.17 m (2H, 6-H, 9-H). Mass spectrum, m/z (I_{rel}, %): 389 (45) $[M]^+$, 346 (100) $[M - C_3H_7]^+$, 330 (78) $[M - OC_3H_7]^+$, 318 (12) $[M - C_4H_8NH]^+$, 304 (31), 249 (9), 70 (10) $[C_4H_8N]^+$, 43 (58) $[C_3H_7]^+$. Found, %: C 73.79; H 5.87; N 3.62. $C_{24}H_{23}NO_4$. Calculated, %: C 74.02; H 5.95; N 3.60. M 389.16.

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