Synthesis of 4-alkyl-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-triones and 3-alkyl-5-arylamino-2-chloromethyl-3*H*-anthra[1,2-*d*]imidazole-6,11-diones based on reactions of 1-amino-9,10-anthraquinones with chloroacetyl chloride

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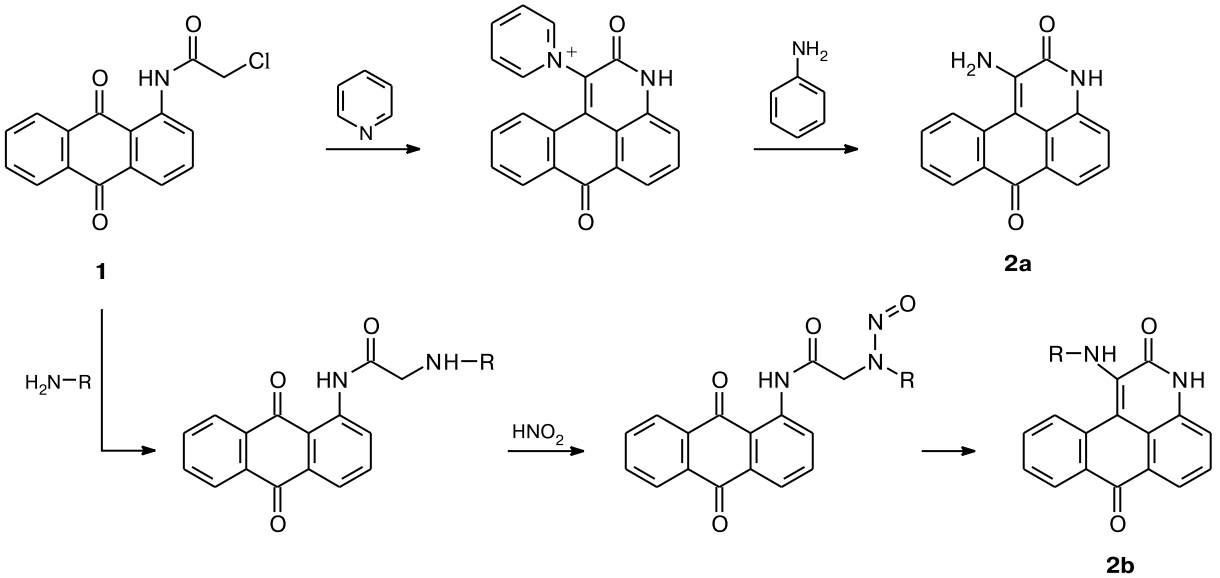
A method was developed for the synthesis of 4-alkyl-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-triones starting from 1-chloroacetylamino-2-halo-9,10-anthraquinones and primary and secondary amines. The reactions of 1-amino-2-alkylamino-9,10-anthraquinones with chloroacetyl chloride afforded 3-alkyl-5-arylamino-2-chloromethyl-3*H*-anthra[1,2-*d*]-imidazole-6,11-diones. The reaction products contain chloroalkyl groups, which can undergo further modifications.

Key words: anthraquinones, heterocycles, 1,2-heterocyclization, imidazoles, quinoid heterocycles, quinoxalines.

It is known that 1-chloroacetylamino-9,10-anthraquinone **1** is a convenient precursor for the synthesis of 1-amino-3*H*-naphtho[1,2,3-*de*]quinoline-2,7-diones (**2a,b**),[1,2] which hold promise for the practical application as luminophores[3] (Scheme 1).

The fact that amino derivatives of 1-chloroacetylamino-9,10-anthraquinones easily undergo 1,9-heterocyclization is attributed to the high CH-acidity of the methylene group. The 1,2-heterocyclization of 1-chloroacetylamino-9,10-anthraquinone derivatives is almost un-

Scheme 1



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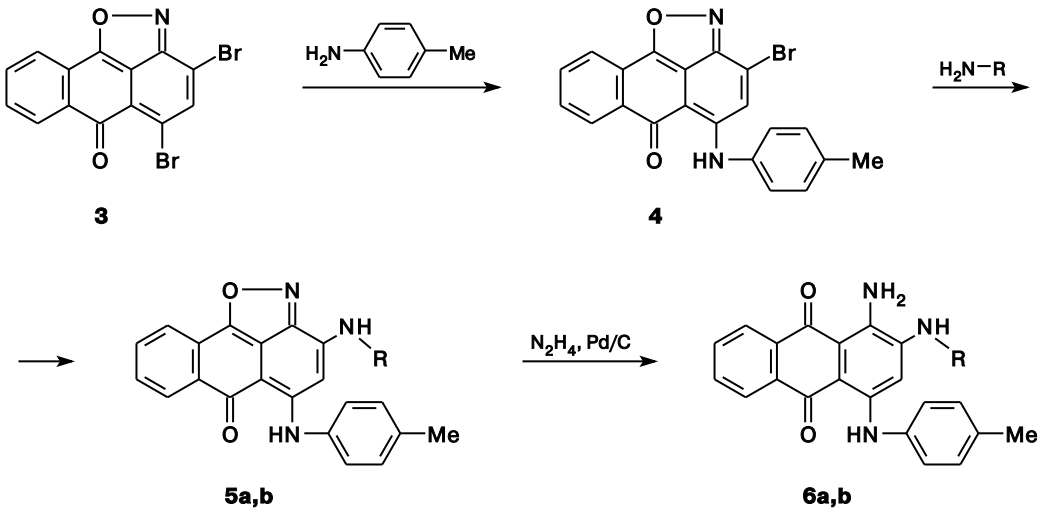
Scheme 2



R = Bu^i (**a**), CH_2Ph (**b**)

known. Only the reaction of 1,2-diamino-9,10-anthraquinone with chloroacetyl chloride giving 2-chloromethyl-2,3,6,11-tetrahydro-1*H*-anthra[1,2-*d*]imidazole-6,11-dione in low yield was described, and this reaction product was used for the synthesis of potent biologically active compounds.[4]

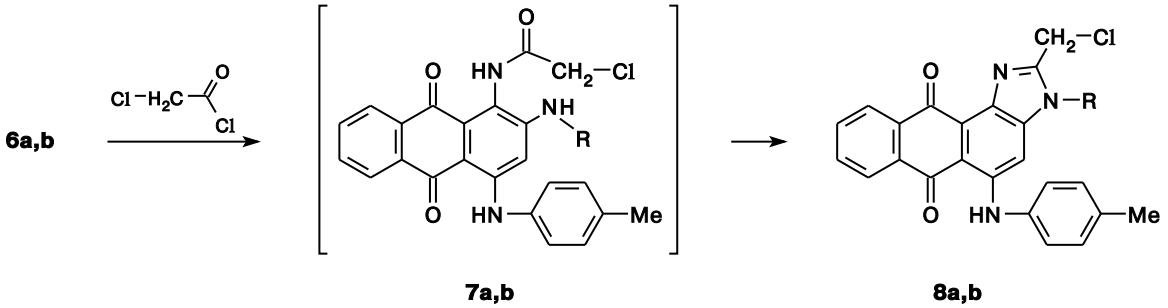
We studied the heterocyclization of 1-amino-9,10-anthraquinone derivatives containing the alkylamino group or the halogen atom in position 2.

The successive amination of 3,5-dibromo-6*H*-[1,9-*cd*]isoxazol-6-one (**3**) reactive toward nucleophiles[5] (Scheme 2) gave amines **6a,b**.

Amines **6a,b** were transformed into 3-alkyl-2-chloromethyl-5-(4-methylphenyl)amino-3*H*-anthra[1,2-*d*]imidazole-6,11-diones **8a,b** upon heating in benzene with chloroacetyl chloride (Scheme 3).

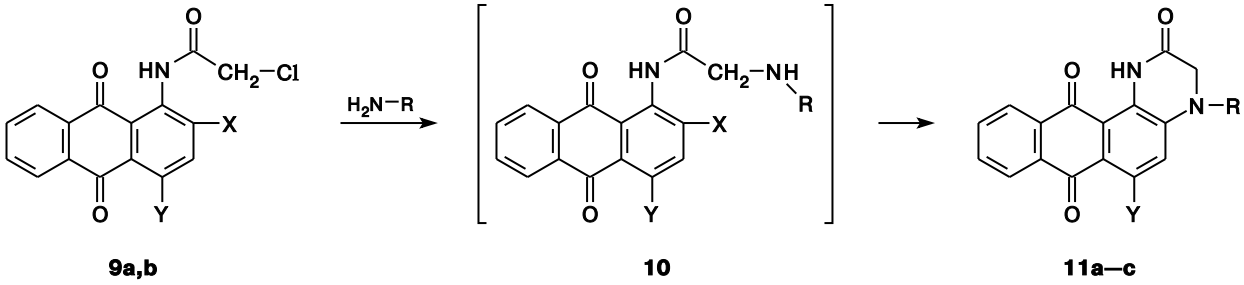
Red-violet products were detected by TLC in the course of the reaction **6**→**8**. The spectrophotometric study confirmed that the reaction of 1-amino-2-benzylamino-4-(4-methylphenyl)amino-9,10-anthraquinone (**6b**) (λ_{max} = = 595 nm) with chloroacetyl chloride initially gives a product with an absorption maximum at 535 nm followed by the formation of final imidazole **8b** (λ_{max} = 550 nm). The hypsochromic shift (~60 nm) observed upon acylation of the starting compound **6b** indicates that it is the primary amino group that is involved in the reaction. The acylation of product **6b** at the benzylamino group would not disturb the 1-amino-4-arylamino-9,10-anthraquinone chromophoric system and would lead to the bathochromic shift of the long-wavelength absorption maximum.[6] According to the UV spectroscopic data, 2-benzylamino-1-chloroacetylamino-4-(4-methylphenyl)amino-9,10-anthraquinone (**7b**) was formed as the intermediate in the course of the reaction of amine **6b** with chloroacetyl chloride in diethyl ether. We failed to isolate this intermediate in the pure form. On heating under reflux in ethyl cellosolve, compound **7b** was also transformed into imidazole **8b**. Consequently, the for-

Scheme 3



R = Bu^i (**a**), CH_2Ph (**b**)

Scheme 4



9a,b **10** **11a—c**

9: X = Cl, Y = H (**a**); X = Br, Y = 4-Me—C_6H_4NH
11: R = CH_2Ph, Y = H (**a**); R = Bu^i, Y = H (**b**); R = CH_2Ph, Y = 4-Me—C_6H_4NH (**c**)

mation of imidazoles **8** from amines occurs according to Scheme 3.

We found that the reaction of 1-chloroacetylamino-2-halo-9,10-anthraquinones with amines (Scheme 4) gives alternative cyclization products of amides **7**, *viz.*, 4-alkyl-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-triones (**11a—c**).

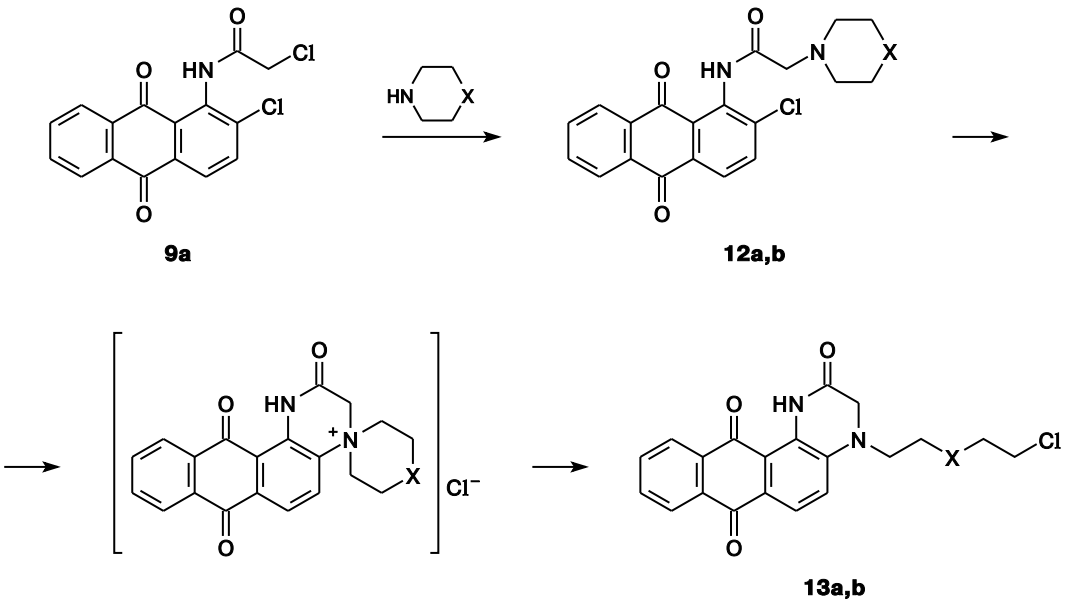
This pathway of the heterocyclization apparently involves the initial nucleophilic substitution of the exocyclic chlorine atom in substrates **9a,b** followed by the closure of the quinoxaline ring in intermediates **10**.

This reaction pathway is confirmed by the fact that we isolated product **12a** as a result of the replacement of the exocyclic chlorine atom in the reaction of chloroacetylaminoanthraquinone **9a** with morpholine, and this product was transformed into the corresponding quinoxaline even upon heating under reflux in ethyl cellosolve for a short time. Apparently, the formation of compounds **13a,b** occurs according to Scheme 5.

The reactions giving compounds **12** and their cyclization products, *viz.*, 4-(ω-chloroalkyl)-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-triones (**13**), can be performed as the one-pot synthesis, as we showed by the transformation **9a**→**12b**→**13b**.

The reaction products, 3-alkyl-5-arylamino-2-chloromethyl-3*H*-anthra[1,2-*d*]imidazole-6,11-diones (**8a,b**) and 4-(ω-chloroalkyl)-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-triones (**13a,b**), contain the chloroalkyl group and may be of interest for the synthesis of biologically active compounds.

Scheme 5



9a **12a,b** **13a,b**

12: X = O (**a**), CH_2 (**b**)

Experimental

The ^{1}H NMR spectra were recorded on a Bruker DRX instrument (500 MHz) in DMSO-d_6 with Me_4Si as the internal standard. The molecular weights of the reaction products were confirmed by mass spectrometry on a Finnigan MAT 8200 instrument. The UV spectra were measured on an Evolution 300 instrument in toluene. The course of the reactions was monitored and the purity of the reaction products was checked by TLC on Silufol UV-254 plates with the use of a toluene—acetone mixture (4 : 1) as the eluent. The melting points were measured on a Boetius hot-stage apparatus.

1-Amino-2-isobutylamino-4-(4-methylphenyl)amino-9,10-anthraquinone (6a). Compound **5a** (1 g, 0.0024 mol) was stirred in a mixture of DMF (10 mL) and EtOH (10 mL) in the presence of Pd/C (0.15 g). Then hydrazine hydrate (1 mL) was added dropwise to the reaction mixture, and the mixture was refluxed for 1 h. The blue-violet precipitate was filtered off hot, washed with EtOH, and dried. The yield was 0.8 g (79%), m.p. 214—216 °C. ^{1}H NMR, δ: 0.93 (d, 6 H, $CH_2CH(\underline{CH_3})_2$, J = 6.6 Hz); 1.91 (m, 1 H, $CH_2\underline{CH}(CH_3)_2$); 2.32 (s, 3 H, Ph$\underline{Me}$); 2.89 (t, 2 H, $\underline{CH_2}CH(CH_3)_2$, J = 6.0 Hz); 6.36 (s, 1 H, H(3)); 6.89 (t, 1 H, $\underline{NH}Bu^i$, J = 6.0 Hz); 7.23 (s, 4 H, $\underline{Ph}Me$); 7.77 (t, 1 H, H(8), J = 7.3 Hz); 7.79 (t, 1 H, H(7), J = 7.3 Hz); 8.26 (d, 2 H, H(6), H(9), J = 7.3 Hz); 9.00 (br.s, 2 H, NH_2); 13.01 (s, 1 H, NH). Found (%): C, 75.01; H, 6.22; N, 10.46. $C_{25}H_{25}N_3O_2$. Calculated (%): C, 75.19; H, 6.27; N, 10.53. UV (toluene), λ_{max}/nm (log ε): 554 (4.07), 593 (4.07).

1-Amino-2-benzylamino-4-(4-methylphenyl)amino-9,10-anthraquinone (6b). The synthesis was carried out analogously to that described above starting from **5b** (0.25 g, 0.00058 mol). The yield of product **6b** was 0.2 g (81%), m.p. 241—243 °C. ^{1}H NMR, δ: 2.30 (s, 3 H, Ph$\underline{Me}$); 4.40 (d, 2 H, $\underline{CH_2}Ph$, J = 5.3 Hz); 6.28 (s, 1 H, H(3)); 6.82 (d, 2 H, H(3′), H(5′), J = 8.3 Hz); 7.07 (d, 2 H, H(2′), H(6′), J = 8.3 Hz); 7.24 (d, 2 H, *o*-Ph, J = 7.2 Hz); 7.32 (t, 1 H, *p*-Ph, J = 7.2 Hz); 7.38 (t, 2 H, *m*-Ph, J = 7.2 Hz); 7.57 (t, 1 H, $\underline{NH}Bn$, J = 5.3 Hz); 7.74 (t, 1 H, H(8), J = 7.3 Hz); 7.77 (t, 1 H, H(7), J = 7.3 Hz); 8.24 (d, 1 H, H(9), J = 7.3 Hz); 8.26 (d, 1 H, H(6), J = 7.3 Hz); 8.92 (s, 2 H, NH_2); 12.93 (s, 1 H, NH). Found (%): C, 77.55; H, 5.29; N, 9.6. $C_{28}H_{23}N_3O_2$. Calculated (%): C, 77.59; H, 5.31; N, 9.69. UV (toluene), λ_{max}/nm (log ε): 557 (4.11), 595 (4.11).

2-Benzylamino-4-(4-methylphenyl)amino-1-chloroacetylamino-9,10-anthraquinone (7b). Compound **6b** (0.87 g, 0.002 mol) was kept in anhydrous diethyl ether (30 mL) with chloroacetyl chloride (0.34 g, 0.003 mol) for 30 min. The precipitate was filtered off and washed with Et_2O. The yield was 0.6 g (60%).

Unfortunately, attempts to isolate product **7b** in the pure form failed. Upon heating or chromatography, product **7b** was transformed into **8b**. UV (toluene), λ_{max}/nm: 535.

2-Chloromethyl-3-isobutyl-5-(4-methylphenyl)amino-3*H*-anthra[1,2-*d*]imidazole-6,11-dione (8a). Compound **6a** (1 g, 0.0025 mol) was heated in benzene (15 mL). Then chloroacetyl chloride (1 mL) was added dropwise. The reaction mixture was refluxed for 3 h. The violet precipitate that formed after cooling was filtered off, washed with benzene and Et_2O, and purified by recrystallization from toluene. The yield was 0.61 g (54%), m.p. 214—215 °C. ^{1}H NMR ($CDCl_3$), δ: 0.97 (d, 6 H, $CH_2CH(\underline{CH_3})_2$, J = 6.0 Hz); 2.45 (m, 1 H, $CH_2\underline{CH}(CH_3)_2$); 2.42 (s, 3 H, Ph$\underline{Me}$); 4.03 (d, 2 H, $\underline{CH_2}CH(CH_3)_2$, J = 7.2 Hz); 5.27 (s, 2 H, CH_2Cl); 7.22 (d, 2 H, H(3′), H(5′), J = 7.7 Hz); 7.26 (d, 2 H, H(2′), H(6′), J = 7.7 Hz); 7.72 (t, 1 H, H(8), J = 7.2 Hz); 7.77 (t, 1 H, H(9), J = 7.2 Hz); 9.23 (br.d, 2 H, H(7), H(10), J = 7.2 Hz); 11.37 (s, 1 H, NH). Found (%): C, 70.73; H, 5.22; N, 8.76. $C_{27}H_{24}ClN_3O_2$. Calculated (%): C, 70.82; H, 5.24; N, 9.19. MS (EI, 70 eV), m/z (I_{rel} (%)): 457 $[M]^+$ (8.91), 423 $[M - Cl + H]^+$ (100), 367 $[M - CH_2Cl - CH(Me)_2 + 2H]^+$ (10.11), 366 $[M - CH_2Cl - CH(Me)_2 + H]^+$ (9.81).

3-Benzyl-2-chloromethyl-5-(4-methylphenyl)amino-3*H*-anthra[1,2-*d*]imidazole-6,11-dione (8b). The synthesis was carried out analogously to that described above starting from **6b** (1 g, 0.0023 mol). The yield of **8b** was 0.66 g (62%), m.p. 219—220 °C. ^{1}H NMR, δ: 2.32 (s, 3 H, Ph$\underline{Me}$); 5.21 (s, 2 H, CH_2Cl); 5.21 (s, 2 H, $\underline{CH_2}Ph$); 6.93 (d, 2 H, H(3′), H(5′), J = 7.7 Hz); 7.12 (d, 2 H, H(2′), H(6′), J = 7.7 Hz); 7.19 (d, 2 H, *o*-Ph, J = 7.2 Hz); 7.26 (s, 1 H, H (4)); 7.37 (m, 3 H, *m*-, *p*-Ph); 7.88 (m, 2 H, H(8), H(9)); 8.13 (m, 1 H, H(7)); 8.22 (m, 1 H, H(10)); 11.25 (s, 1 H, NH). Found (%): C, 73.30; H, 4.48; N, 8.55. $C_{30}H_{22}ClN_3O_2$. Calculated (%): C, 73.24; H, 4.47; N, 8.54. MS (EI, 70 eV), m/z (I_{rel} (%)): 491 $[M]^+$ (3.30), 456 $[M - Cl]^+$ (5.21), 364 $[M - Cl - H - PhCH_2]^+$ (5.81), 91 $[PhCH_2]^+$ (100).

2-Chloro-1-chloroacetylamino-9,10-anthraquinone (9a). 1-Amino-2-chloro-9,10-anthraquinone (5.1 g, 0.02 mol) was refluxed in benzene (40 mL) with chloroacetyl chloride (5 mL) for 3 h. The precipitate that formed after cooling was filtered off, washed with benzene and Et_2O, and purified by recrystallization from AcOH. The yield was 5.2 g (78%), m.p. 185—186 °C. ^{1}H NMR ($CDCl_3$), δ: 4.30 (s, 2 H, CH_2Cl); 7.80 (m, 2 H, H(6), H(7)); 7.86 (d, 1 H, H(3), J = 7.9 Hz); 8.21 (d, 1 H, H(4), J = 7.9 Hz); 8.25 (m, 2 H, H(5), H(8)); 10.49 (s, 1 H, NH). Found (%): C, 57.86; H, 2.78; N, 4.36. $C_{16}H_9Cl_2NO_3$. Calculated (%): C, 57.49; H, 2.69; N, 4.19.

2-Bromo-1-chloroacetylamino-4-(4-methylphenyl)amino-9,10-anthraquinone (9b). 1-Amino-2-bromo-4-(4-methylphenyl)-amino-9,10-anthraquinone[7] (6.1 g, 0.015 mol) was refluxed in benzene (80 mL) with chloroacetyl chloride (6 mL) for 3 h. The precipitate that formed after cooling was filtered off, washed with benzene and Et_2O, and purified by recrystallization from *o*-xylene. The yield was 6.2 g (86%), m.p. 198—199 °C. ^{1}H NMR ($CDCl_3$), δ: 2.49 (s, 3 H, Ph$\underline{Me}$); 4.25 (s, 2 H, CH_2Cl); 7.17 (d, 2 H, H(3′), H(5′), J = 7.8 Hz); 7.24 (d, 2 H, H(2′), H(6′), J = 7.8 Hz); 7.66 (s, 1 H, H(3)); 7.74 (t, 1 H, H(6 or 7), J = 7.3 Hz); 7.78 (t, 1 H, H(6 or 7), J = 7.3 Hz); 8.18 (d, 1 H, H(5 or 8), J = 7.3 Hz); 8.25 (d, 1 H, H(5 or 8), J = 7.3 Hz); 10.04 (s, 1 H, NHCO); 11.47 (s, 1 H, NH). Found (%): C, 57.68; H, 3.32; N, 6.08. $C_{23}H_{16}BrClN_2O_3$. Calculated (%): C, 57.08; H, 3.31; N, 5.79.

4-Benzyl-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-trione (11a). Compound **9a** (0.67 g, 0.002 mol) was dissolved in dioxane (10 mL). Then benzylamine (1 mL) was added. The reaction mixture was refluxed for 1 h, water (5 mL) was added, and the reaction mixture was cooled. The dark-cherry precipitate that formed was filtered off, washed with aqueous EtOH, and recrystallized from ethyl cellosolve. The yield was 0.5 g (71%), m.p. 201—202 °C. ^{1}H NMR, δ: 4.24 (s, 2 H, H(3)); 4.71 (s, 2 H, $\underline{CH_2}Ph$); 7.12 (d, 1 H, H(5), J = 8.2 Hz); 7.30 (m, 1 H, *p*-Ph); 7.37 (m, 4 H, *o*-, *m*-Ph); 7.75 (d, 1 H, H(6), J = 8.2 Hz); 7.90 (m, 2 H, H(9), H(10)); 8.15 (m, 1 H, H(8)); 8.23 (m, 1 H, H(11)); 11.89 (s, 1 H, NH). Found (%): C, 74.68; H, 4.35; N, 7.40. $C_{23}H_{16}N_2O_3$. Calculated (%): C, 75.00; H, 4.35; N, 7.60. MS (EI, 70 eV), m/z (I_{rel} (%)): 368 $[M]^+$ (33.03), 277

$[M - PhCH_2]^+$ (10.71), 249 $[M - PhCH_2NCH_2]^+$ (16.72), 91 $[PhCH_2]^+$ (100).

4-Isobutyl-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-trione (11b). The synthesis was carried out analogously to that described above starting from **9a** (0.65 g, 0.002 mol) and isobutylamine (1 mL). The yield was 0.58 g (89%), m.p. 214—215 °C. ^{1}H NMR, δ: 0.95 (d, 6 H, $CH_2CH(\underline{CH_3})_2$, J = 6.6 Hz); 2.10 (m, 1 H, $CH_2\underline{CH}(CH_3)_2$); 3.24 (d, 2 H, $\underline{CH_2}CH(CH_3)_2$, J = 7.5 Hz); 4.21 (s, 2 H, H(3)); 7.16 (d, 1 H, H(5), J = 8.7 Hz); 7.80 (d, 1 H, H(6), J = 8.7 Hz); 7.87 (t, 1 H, H(9), J = 7.3 Hz); 7.90 (t, 1 H, H(10), J = 7.3 Hz); 8.13 (d, 1 H, H(8), J = 7.3 Hz); 8.19 (d, 1 H, H(11), J = 7.3 Hz); 11.89 (s, 1 H, NH). Found (%): C, 71.09; H, 5.41; N, 8.50. $C_{20}H_{18}N_2O_3$. Calculated (%): C, 71.86; H, 5.39; N, 8.38. MS (EI, 70 eV), m/z (I_{rel} (%)): 334 $[M]^+$ (22.82), 291 $[M - CH(Me)_2]^+$ (100), 264 $[M - CH(Me)_2 - CO + H]^+$ (45.65), 263 $[M - CH(Me)_2 - CO]^+$ (80.18).

4-Benzyl-6-(4-methylphenyl)amino-3,4-dihydronaphtho[2,3-*f*]-quinoxaline-2,7,12-(1*H*)-trione (11c). The synthesis was carried out analogously to that described above starting from **9b** (0.9 g, 0.002 mol) and benzylamine (1 mL) at 60—80 °C for 1 h. The blue precipitate that formed was filtered off, washed with aqueous EtOH, and purified by recrystallization from butan-1-ol. The yield was 0.6 g (75%), m.p. 205—206 °C. ^{1}H NMR, δ: 2.30 (s, 3 H, Ph$\underline{Me}$); 4.40 (s, 2 H, H(3)); 4.51 (s, 2 H, $\underline{CH_2}$Ph); 6.37 (s, 1 H, H(5)); 6.81 (d, 2 H, H(3′), H(5′), J = 8.3 Hz); 7.05 (d, 2 H, H(2′), H(6′), J = 8.3 Hz); 7.21 (d, 2 H, *o*-Ph); 7.35 (m, 3 H, *m*-, *p*-Ph); 7.81 (t, 1 H, H(9), J = 7.3 Hz); 7.89 (t, 1 H, H(10), J = 7.3 Hz); 8.21 (br.d, 2 H, H(8), H(11), J = 7.3 Hz); 12.12 (s, 1 H, NHCO); 12.51 (s, 1 H, NH). Found (%): C, 76.61; H, 4.91; N, 8.68. $C_{30}H_{23}N_3O_3$. Calculated (%): C, 76.11; H, 4.86; N, 8.88. MS (EI, 70 eV), m/z (I_{rel} (%)): 473 $[M]^+$ (77.88), 381 $[M - PhCH_2 - H]^+$ (26.03), 354 $[M - PhCH_2 - CO]^+$ (32.13), 91 $[PhCH_2]^+$ (100).

2-Chloro-1-morpholinoacetylamino-9,10-anthraquinone (12a). Compound **9a** (0.5 g, 0.0015 mol) in dioxane (6 mL) containing morpholine (1 mL) was kept at 20—25 °C for 1 h. After completion of the reaction, the mixture was poured onto ice and filtered. The precipitate that formed was washed with water and aqueous EtOH and purified by recrystallization from toluene. The yield was 0.35 g (61%), m.p. 161—163 °C. ^{1}H NMR ($CDCl_3$), δ: 2.77 (t, 4 H, NCH_2, J = 3.9 Hz); 3.28 (s, 2 H, $COCH_2N$); 3.96 (t, 4 H, OCH_2, J = 4.6 Hz); 7.80 (m, 2 H, H(7), H(8)); 7.85 (d, 1 H, H(3), J = 8.4 Hz); 8.20 (m, 2 H, H(4), H(6)); 8.26 (m, 1 H, H(9)); 10.75 (s, 1 H, NH). Found (%): C, 62.42; H, 4.42; N, 7.33. $C_{20}H_{17}ClN_2O_4$. Calculated (%): C, 62.42; H, 4.42; N, 7.28. MS (EI, 70 eV), m/z (I_{rel} (%)): 384 $[M]^+$ (0.50), 356 $[M - CO]^+$ (0.50), 257 $[M - C_4H_8NOCH_2CO + H]^+$ (6.91), 164 $[M - C_4H_8NOCH_2 - 3\,CO - Cl - H]^+$ (21.02), 100 $[C_4H_8NOCH_2]^+$ (100).

4-(5-Chloro-3-oxapentyl)-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-trione (13a). A solution of compound **12a** (0.38 g, 0.001 mmol) in ethyl cellosolve was refluxed for 5 min. The resulting dark-cherry precipitate was filtered off, washed with aqueous EtOH and Et_2O, and recrystallized from butan-1-ol. The yield was 0.26 g (68%). ^{1}H NMR, δ: 3.64 (t, 2 H, OCH_2, J = 5.3 Hz); 3.72 (m, 4 H, NCH_2CH_2O); 3.77 (t, 2 H, CH_2Cl, J = 5.3 Hz); 4.29 (s, 2 H, H(3)); 7.16 (d, 1 H, H(5), J = 8.8 Hz); 7.78 (d, 1 H, H(6), J = 8.8 Hz); 7.88 (m, 2 H, H(9), H(10)); 8.12 (d, 1 H, H(8), J = 7.3 Hz); 8.17 (d, 1 H, H(11), J = 7.3 Hz); 11.85 (s, 1 H, NH). Found (%): C, 62.05; H, 4.57; N, 7.39. $C_{20}H_{17}ClN_2O_4$. Calculated (%): C, 62.42; H, 4.42; N, 7.28. MS (EI, 70 eV), m/z (I_{rel} (%)): 384 $[M]^+$ (20.92), 291 $[M - CH_2OCH_2CH_2 - Cl]^+$ (81.08), 264 $[M - CH_2OCH_2CH_2 - Cl - CO + H]^+$ (21.42), 263 $[M - CH_2OCH_2CH_2 - Cl - CO]^+$ (100).

4-(5-Chloropentyl)-3,4-dihydronaphtho[2,3-*f*]quinoxaline-2,7,12-(1*H*)-trione (13b). A solution of compound **9a** (0.38 g, 0.001 mol) in dioxane (5 mL) containing piperidine (1 mL) was refluxed for 1 h. After completion of the reaction, the cold mixture was poured onto ice. The precipitate that formed was filtered, washed with aqueous EtOH and Et_2O, and recrystallized from ethyl cellosolve. The yield was 0.28 g (73%), m.p. 199—201 °C. ^{1}H NMR, δ: 1.48 (m, 2 H, CH_2(3′)); 1.64 (m, 2 H, CH_2(2′)); 1.79 (m, 2 H, CH_2(4′)); 3.40 (t, 2 H, CH_2(1′), J = 7.6 Hz); 3.66 (t, 2 H, CH_2(5′)); 7.10 (d, 1 H, H(5), J = 8.6 Hz); 7.81 (d, 1 H, H(6), J = 8.6 Hz); 7.88 (m, 2 H, H(9), H(10)); 8.13 (d, 1 H, H(8), J = 7.3 Hz); 8.18 (d, 1 H, H(11), J = 7.3 Hz); 11.85 (s, 1 H, NH). Found (%): C, 65.88; H, 4.97; N, 7.32. $C_{21}H_{19}ClN_2O_3$. Calculated (%): C, 65.64; H, 4.88; N, 7.30. MS (EI, 70 eV), m/z (I_{rel} (%)): 382 $[M]^+$ (36.84), 346 $[M - Cl - H]^+$ (7.11), 291 $[M - CH_2CH_2CH_2CH_2 - Cl]^+$ (68.97), 264 $[M - CH_2CH_2CH_2CH_2CH_2 - Cl - CO + H]^+$ (22.32), 263 $[M - CH_2CH_2CH_2CH_2 - Cl - CO]^+$ (100).

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