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STUDY OF THE PRODUCTS FROM REACTION OF 1(2)-AMINOANTHRAQUINONES WITH 1-CHLORO-2,3-EPOXYPROPANE

V. Getautis, M. Dashkyavichene, I. Paulauskaite, and A. Stanisauskaite

1(2)-(3-Chloro-2-hydroxypropylamino)anthraquinones were synthesized by the reaction of 1(2)-aminoanthraquinones with 1-chloro-2,3-epoxypropane and were then subjected to various transformations.

Keywords: 1(2)-aminoanthraquinone, aniline, 1,3-benzenedithiol, 1-chloro-2,3-epoxypropane, diethylamine, dioxolane, isopropylamine, piperidine, pyridine.

Anthraquinone and its compounds are widely used for the production of organic dyes, pigments, and luminophores, for the synthesis of drugs, and as catalysts, analytical reagents, monomers, antioxidants, agents for the protection of plants, photoresistors, etc. In the electrophotographic process electronic conductivity has many advantages compared with hole conductivity, but the arsenal of compounds distinguished by good electron transport is still small, and the search for such compounds is particularly urgent at the present time. Since there are among electron-transporting materials (ETM) compounds containing a keto group, e.g., derivatives of diphenoquinone, naphthalenedione [1, 2], etc., compounds containing carbonyl groups, namely 1(2)-aminoanthraquinones, were used as starting materials for the synthesis of ETMs. The aim of the present work was to synthesize ETMs with improved physicochemical properties. This aim was achieved by inserting an aliphatic chain into the structure of the ETM using the products from reaction of 1(2)-aminoanthraquinone with 1-chloro-2,3-epoxypropane (CEP). During the action of an excess of CEP on 1-aminoanthraquinone in the presence of 85% acetic acid only the mono derivative 1-(3-chloro-2-hydroxypropylamino)anthraquinone **1a** was isolated from the reaction mixture. In this case the bis derivative is not formed, as explained by the appearance of a hydrogen bond between the carbonyl oxygen and the hydrogen of the *peri*-amino group [3]. The corresponding mono and bis derivatives, i.e., 2-(3-chloro-2-hydroxypropylamino)anthraquinone (**1b**) and 2-[bis(3-chloro-2-hydroxypropyl)amino]anthraquinone (**2**), were obtained from 2-aminoanthraquinone under analogous conditions (Scheme 1).

The discovery of two sets of signals for the hydroxy group during analysis of the ^{1}H NMR spectrum of compound **2** indicates the existence of a diastereomeric mixture.

Treatment of the solutions of **1a**,**b** and **2** in dioxane with 85% powdered potassium hydroxide gave the corresponding epoxy compounds 1(2)-(2,3-epoxypropylamino)anthraquinones **3a**,**b** and 2-(2,3-epoxypropyl-amino)anthraquinone (**4**). In addition to the above-mentioned reaction, other reactions characteristic of 3-chloro-2-hydroxypropyl compounds with piperidine, pyridine, diethylamine, isopropylamine, and potassium cyanide were also carried out in order to confirm the structure of compounds **1a**,**b**. Here the following compounds were

Kaunas Technological University, Kaunas, Lithuania; e-mail: alsta@ktu.lt. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 505-516, April, 2005. Original article submitted July 20, 2004.

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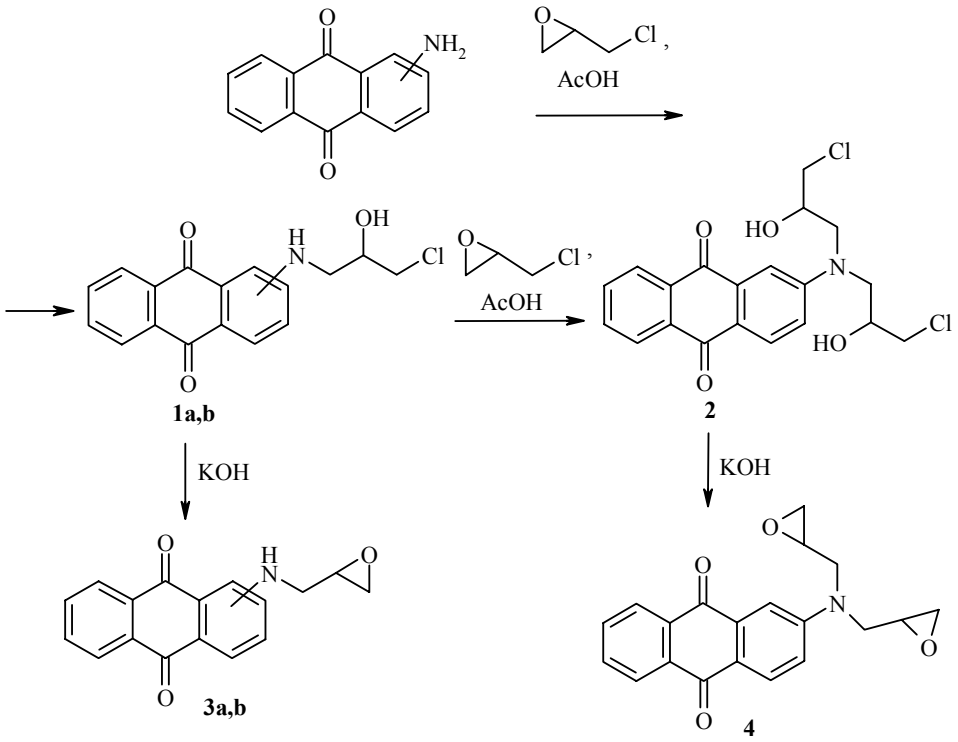
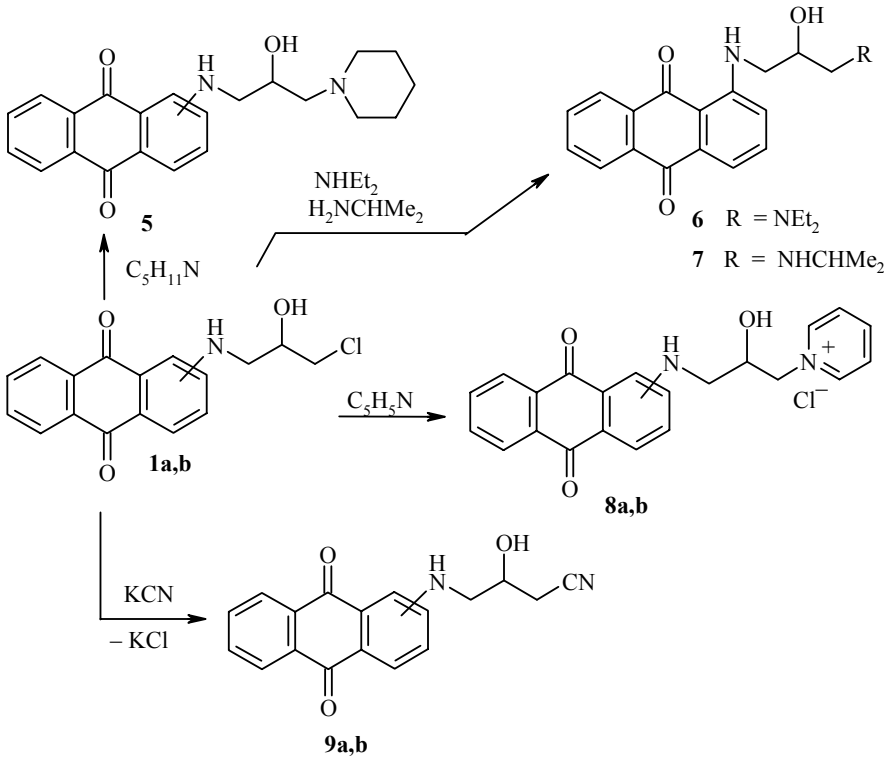
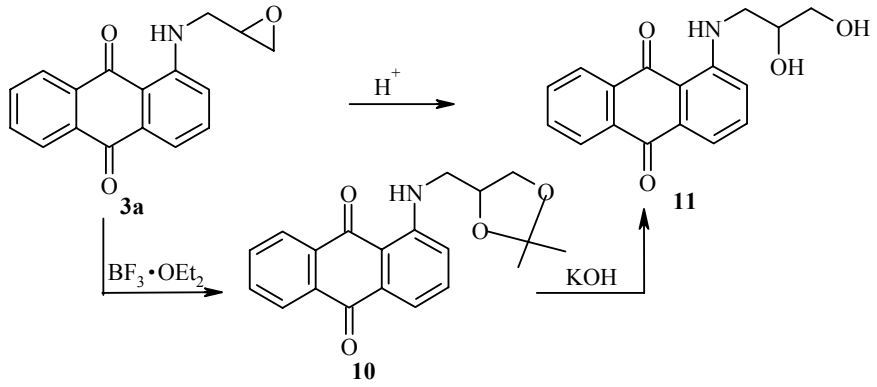
Scheme 1



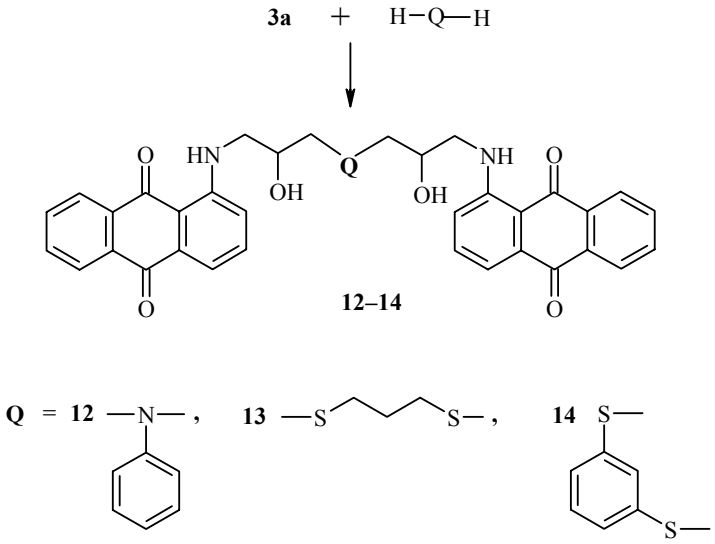
obtained: 1-(2-Hydroxy-3-piperidinopropylamino)anthraquinone (**5**), 1-(3-diethylamino-2-hydroxypropyl-amino)anthraquinone (**6**), 1-(2-hydroxy-3-isopropylamino)anthraquinone (**7**), 1-[3-(anthraquinone-1(2)-amino)-2-hydroxypropyl]pyridinium chlorides (**8a**,**b**), 4-[anthraquinone-1(2)-amino]-3-hydroxybutanenitriles (**9a**,**b**).



The structure of the epoxy compound **3a** was confirmed by reactions leading to the formation of dioxolane and propanediol derivatives. During the action of dilute sulfuric acid on **3a** (method A) 1-(2,3-dihydroxypropylamino)anthraquinone (**11**) was only isolated from the reaction mixture after chromatographic purification. The action of acetone in the presence of $BF_3 \cdot OEt_2$ catalyst gave 1-(2,2-dimethyl-1,3-dioxolane-4-methylamino)anthraquinone (**10**). When a solution of the latter in butanol was boiled in the presence of powdered 85% potassium hydroxide (method B), the fairly pure diol **11** was formed readily, i.e., method A is more suitable for the synthesis of compound **11**.



During investigation of the electrophotographic properties of N-2,3 epoxypropyl and other derivatives of 1- and 2-aminoanthraquinones it was established that only the derivatives of 1-aminoanthraquinone are distinguished by electron transfer, while most of them are well crystallizing substances, hindering the production of good-quality films. In order to eliminate this disadvantage the following dimeric compounds were synthesized according to the procedure described in [4] by the action of aniline, 1,3-propanedithiol, and 1,3-benzenedithiol on compound **3a**: N,N-Bis[1-(anthraquinone-1-amino)-2-hydroxypropyl]aniline (**12**), 1,11-di(anthraquinone-1-amino)-2,10-dihydroxy-4,8-dithiaundecane (**13**), and bis[3-(anthraquinone-1-amino)-2-hydroxypropylthio]benzene (**14**).



In the case of 1,3-benzenedithiol nucleophilic opening of the oxirane ring takes place even at room temperature. The dimers **12** and **13** are crystalline substances. After chromatographic purification and reprecipitation (by pouring a 20% solution into a tenfold excess of hexane) the dimer **14** was obtained in the

TABLE 1. The Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				mp, °C (vp, °C)	Solvent for crystallization	Yield, %
		C	H	N	Cl			
1	2	3	4	5	6	7	8	9
1a	$C_{17}H_{14}ClNO_3$	64.56 / 64.67	4.75 / 4.69	4.49 / 4.43	11.35 / 11.23	168.5-169.5 168 [4]	1,4-Dioxane–2-propanol	63.5
1b	$C_{17}H_{14}ClNO_3$	64.75 / 64.67	4.53 / 4.69	4.58 / 4.43	11.40 / 11.23	185-186 184.5 [4]	" "	53.5
2	$C_{20}H_{19}Cl_2NO_4$	58.69 / 58.84	4.75 / 4.69	3.52 / 3.43	17.52 / 17.37	177-178 176 [3]	" "	41.4
3a	$C_{17}H_{13}NO_2$	73.26 / 73.11	4.79 / 4.69	5.18 / 5.01	—	158.5-160	1,4-Dioxane	87.5
3b	$C_{17}H_{13}NO_2$	73.27 / 73.11	4.78 / 4.69	5.17 / 5.01	—	191-192	" "	79.1
4	$C_{20}H_{17}NO_4$	71.45 / 73.11	5.02 / 5.11	4.25 / 4.18	—	174.5-175.5	2-Propanol	92.7
5	$C_{22}H_{24}N_2O_3$	72.45 / 72.50	6.60 / 6.64	7.78 / 7.69	—	123-124	1,4-Dioxane–2-propanol	79
6	$C_{21}H_{24}N_2O_3$	71.48 / 71.57	6.75 / 6.68	8.10 / 7.95	—	83.5-84	2-Propanol	90.6

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9
7	$C_{20}H_{22}N_2O_3$	70.89 / 70.99	6.42 / 6.55	8.31 / 8.28	—	111.5-112.5	2-Propanol	83.6
8a	$C_{22}H_{19}ClN_2O_3$	66.58 / 66.92	4.93 / 5.09	7.19 / 7.08	8.88 / 8.98	203-204	Methanol–1,4-dioxane	75.8
8b	$C_{22}H_{19}ClN_2O_3$	66.56 / 66.92	4.91 / 5.09	7.24 / 7.08	9.05 / 8.98	251-252	" "	74.5
9a	$C_{18}H_{14}N_2O_3$	70.70 / 70.58	4.75 / 4.61	9.33 / 9.15	—	193-194	1,4-Dioxane–2-propanol	66.8
9b	$C_{18}H_{14}N_2O_3$	70.67 / 70.58	4.70 / 4.61	9.25 / 9.15	—	200.5-201.5	" "	64.4
10	$C_{20}H_{19}NO_4$	71.31 / 71.20	5.79 / 5.68	4.20 / 4.15	—	99-100	2-Propanol	86.4
11	$C_{17}H_{15}NO_4$	68.79 / 68.68	4.88 / 5.09	4.81 / 4.71	—	233-234	" "	90 (A) 86.5 (B)
12	$C_{40}H_{33}N_3O_6$	73.63 / 73.72	5.28 / 5.10	6.76 / 6.45	—	204-210 (90)	Chloroform–2-propanol	80.2
13	$C_{37}H_{34}N_2O_6S_2$	66.54 / 66.65	5.25 / 5.14	4.41 / 4.20	—	125-140 (49)		89.1
14	$C_{40}H_{32}N_2O_6S_2$	68.61 / 68.55	4.51 / 4.61	4.16 / 4.05	—	118-131 (63)		63.3

TABLE 2. The IR and ^{1}H and ^{13}C NMR Spectra of the Synthesized

Com-pound	IR spectrum, ν, cm^{-1}	^{1}H [^{13}C NMR] spectrum, δ, ppm (*J*, Hz)
1	2	3
1a	3497 (OH); 3277 (NH); 3068 ($CH_{arom.}$); 2913, 2868 ($CH_{aliph.}$); 1668, 1623 (C=O)	**$CDCl_3$**, 250 MHz: 9.92 (1H, t, *J* = 5.3, NH); 8.31-8.15 (2H, m, H-5,8); 7.82-7.65 (2H, m, H-6,7); 7.65-7.45 (2H, m, H-3,4); 7.1 (1H, d, *J* = 8.3, H-2); 4.22 (1H, m, C<u>H</u>–OH); 3.85-3.55 (4H, m, C<u>H</u>$_2$CHC<u>H</u>$_2$); 2.3 (1H, s, br, OH)
1b	3657-3121 (OH, NH); 3068 ($CH_{arom.}$); 2949, 2926 ($CH_{aliph.}$); 1668, 1631 (C=O)	**DMSO-d_6**, 250 MHz: 8.20-8.10 (2H, m, H-5,8); 7.97 (1H, d, *J* = 8.5, H-4); 7.93-7.70 (2H, m, H-6,7); 7.39-7.3 (2H, m, NH, H-1); 7.06 (1H, d, split, *J* = 8.6, *J* = 2.5, H-3); 5.55 (1H, d, *J* = 5.05, OH); 3.92 (1H, m, H_X, C<u>H</u>–OH); 3.72 (1H, dd, J_{AX} = 4.5, *cis*-H_A, N–CH_2); 3.68 (center of AB part of ABX system, J_{AB} = 11.5); 3.64 (1H, dd, J_{BX}=5.5, *trans*-H_B, N–CH_2); 3.5–3.2 (2H, m, C<u>H</u>$_2$–Cl)
2	3477 (OH), 3080 ($CH_{arom.}$); 2948, 2914 ($CH_{aliph.}$); 1670, 1634 (C=O)	**DMSO-d_6**, 250 MHz: (mixture of diastereomers) 8.22-8.11 (2H, m, H-5,8); 8.27 (1H, d, *J* = 8.8, H-4); 7.95-7.81 (2H, m, H-6,7); 7.56-7.47 (1H, m, H-1); 7.31-7.19 (1H, m, H-3); 5.60 and 5.54 (2H, dd, *J* = 5.1, OH); 4.12-3.97 (2H, m, C<u>H</u>–OH); 3.89-3.49 (8H, m, C<u>H</u>$_2$CHC<u>H</u>$_2$)
3a	3262 (NH); 3064 ($CH_{arom.}$); 2995, 2924, 2861 ($CH_{aliph.}$); 1663, 1630 (C=O); 956, 915 (def. vib. of epoxy group)	**$CDCl_3$**, 300 MHz: 9.84 (1H, t, *J* = 5.2, NH); 8.32-8.17 (2H, m, H-5,8); 7.81-7.63 (2H, m, H-6,7); 7.63-7.50 (2H, m, H-3,4); 7.13 (1H, d, split, *J* = 8.4, *J* = 1.35, H-2); 3.78-3.68 (2H, m, N–CH_2); 2.88 (1H, dd, J_{BX} = 3.9, *trans*-H_B CH_2 epoxy group); 2.81 (center of AB part of ABX system, J_{AB} = 4.8); 2.75 (1H, dd, J_{AX}=2.7, *cis*-H_A CH_2 epoxy group) [**^{13}C NMR spectrum, $CDCl_3$**, 300 MHz: 185.23, 183.64 (C=O); 151.62; 135.36; 134.79; 134.58; 133.98; 133.08; 132.91; 126.74; 126.71; 117.96; 116.25; 113.39; 50.73 (CH_2<u>C</u>H); 45.11 (CH<u>C</u>H_2); 44.04 (N–CH_2)]
3b	3374 (NH); 3067 ($CH_{arom.}$); 2994, 2923, 2892, 2853 ($CH_{aliph.}$); 1668, 1654 (C=O)	**DMSO-d_6**, 400 MHz: 8.16-8.08 (2H, m, H-5,8); 7.95 (1H, d, *J* = 8.8, H-4); 7.90-7.78 (2H, m, H-6,7); 7.44 (1H, t, *J* = 5.8, NH); 7.31 (1H, d, *J* = 2.8, H-1); 7.05 (1H, d, split, *J* = 8.8, *J* = 2.4, H-3); 3.65-3.22 (2H, m, N–CH_2); 3.19-3.12 (1H, m, NCH_2C<u>H</u>$_X$); 2.77 (1H, dd, J_{BX} = 4.0, *trans*-H_B CH_2 epoxy group); 2.69 (center of AB part of ABX system, *J* = 5.2); 2.62 (1H, dd, J_{AX} = 2.8, *cis*-H_A CH_2 epoxy group) [**^{13}C NMR spectrum, DMSO-d_6**, 400 MHz: 183.33, 180.22 (C=O); 153.89; 134.74; 134.47; 133.71; 133.51; 133.06; 129.48; 126.52; 126.42; 121.42; 117.82; 115.62; 50.47 (CH_2<u>C</u>H); 44.51 (CH<u>C</u>H_2); 44.05 (N–CH_2)]

TABLE 2 (continued)

1	2	3
4	3068, 3001 ($CH_{arom.}$); 2921 ($CH_{aliph.}$); 1669, 1655 (C=O)	**DMSO-d_6**, 100 MHz: 8.28-7.79 (5H, m, H-4,8); 7.59-7.44 (1H, m, H-1); 7.39-7.21 (1H, m, H-3); 4.12-3.40 (4H, m, N–CH_2); 3.41-3.15 (2H, m, C<u>H</u>CH_2); 3.0-2.37 (4H, m, CHC<u>H_2</u>)
5	3387 (OH); 3267 (NH), 3074 ($CH_{arom.}$); 2935, 2847 ($CH_{aliph.}$); 1662, 1635 (C=O)	**$CDCl_3$**, 300 MHz: 9.94 (1H, t, *J* = 5.2, NH); 8.28 (1H, d, split, *J* = 7.2, *J* = 1.8, H-8); 8.21 (1H, d, split, *J* = 7.8, *J* = 1.2, H-5); 7.82-7.43 (4H, m, H-3,4,6,7); 7.1 (1H, d, *J* = 7.8, H-2); 4.10-3.97 (1H, m, OH); 3.52-3.28 (2H, m, N–C<u>H_2</u>); 2.71-2.51 (2H, m, C<u>H_2</u>–NC_5H_{10}); 2.51-2.27 (4H, m, CH_2-2,6 piperidine); 1.72-1.34 (6H, m, CH_2-3,4,5 piperidine) [**^{13}C NMR spectrum, $CDCl_3$**, 300 MHz: 184.97, 183.78 (C=O); 151.88; 135.35; 135.17; 134.67; 133.16; 133.03; 132.84; 126.78; 126.17; 117.93; 115.74; 113.28; 65.28 (CH–OH); 62.17 (N–CH_2); 54.71 (CH_2-2'); 45.7 (<u>C</u>H_2–NC_5H_{10}); 26.13 (CH_2-3'); 24.22 (CH_2-4')]
6	3500-3230 (OH, NH); 3079 ($CH_{arom.}$); 2973, 2909, 2845 ($CH_{aliph.}$); 1665, 1633 (C=O)	**$CDCl_3$**, 300 MHz: 9.83 (1H, m, NH); 8.26 (1H, d, split, *J* = 7.5, *J* = 1.3, H-8); 8.07 (1H, d, split, *J* = 7.5, *J* = 1.5, H-5); 7.64-7.50 (2H, m, H-6,7); 7.48-7.34 (2H, m, H-3,4); 6.95 (1H, d, split, *J* = 7.8, *J* = 1.6, 2-H); 3.86 (1H, m, C<u>H</u>–OH); 3.36-3.14 (2H, m, N–CH_2); 2.61-2.29 (7H, m, C<u>H_2</u>NC<u>H_2</u>CH_3, OH); 0.91 (6H, t, *J* = 7.1, CH_3)
7	3595-3250 (OH); 3298 (NH); 3074 ($CH_{arom.}$); 2970, 2920, 2834 ($CH_{aliph.}$); 1670, 1627 (C=O)	**$CDCl_3$**, 100 MHz, δ, ppm (*J*, Hz): 9.92 (1H, t, NH); 8.38-8.10 (2H, m, H-5,8); 7.84–7.40 (4H, m, H-3,4,6,7); 7.19-6.95 (2H, m, H-2, N<u>H</u>–$CH(CH_3)_2$); 4.19-3.80 (1H, m, C<u>H</u>–OH); 3.52-3.25 (2H, m, N–C<u>H_2</u>); 3.05-2.48 (5H, m, C<u>H</u>(O<u>H</u>)C<u>H_2</u>–N–C<u>H</u>$(CH_3)_2$); 1.10 (6H, d, *J* = 6.5, $CH(CH_3)_2$) [**^{13}C NMR spectrum, $CDCl_3$**, 400 MHz: 184.90, 183.78 (C=O); 151.67; 134.81; 134.47; 134.19; 133.89 132.90; 126.69; 118.00; 115.89; 77.54; 77.23; 76.91; 68.61 (N–<u>C</u>$H(CH_3)_2$); 50.79, 49.17 (<u>C</u>H_2–N–$CH(CH_3)_2$, CH–(<u>C</u>$H_3)_2$); 47.25 (CH–OH); 23.4 (N–CH_2)]
8a	3394 (OH); 3264 (NH); 3059 ($CH_{arom.}$); 2856 ($CH_{aliph.}$); 1674, 1631 (C=O)	**CD_3OD**, 250 MHz: 9.9 (1H, t, *J* = 5.3, NH); 9.04 (2H, m, H-2,6 pyridinium); 8.62 (1H, m, H-4 pyridinium); 8.23-8.00 (4H, m, H-5,8 anthraquinone (AHTP); H-3,5 pyridinium); 7.85-7.60 (2H, m, H-6,7 AHTP); 7.60-7.37 (2H, m, H-3,4 AHTP); 7.28 (1H, d, split, *J* = 8.2, *J* = 1.5, H-2 AHTP); 5.05-4.45 (3H, m, N–CH_2, OH); 4.41-4.20 (1H, m, C<u>H</u>–OH); 3.80-3.45 (2H, m, N–CH_2)
8b	3238 (OH); 3150 (NH); 3061 ($CH_{arom.}$); 2957, 2866 ($CH_{aliph.}$), 1668, 1635 (C=O)	**CD_3OD**, 250 MHz: 9.04 (2H, m, H-2,6 pyridinium); 8.66 (1H, d, *J* = 7.5, H-4 pyridinium); 8.25-7.90 (5H, m, H-4,5,6,7,8 AHTP); 7.9-7.70 (2H, m, H-3,5 pyridinium); 7.38-7.45 (2H, m, NH, H-1 AHTP); 7.07 (1H, d, split, *J* = 8.7, *J* = 2.2, H-3 AHTP); 5.00-4.50 (3H, m, N–CH_2, OH); 4.32-4.18 (1H, m, C<u>H</u>–OH); 3.65-3.40 (2H, m, N–CH_2)
9a	3438 (OH); 3274 (NH); 3080 ($CH_{arom.}$); 2935, 2873 ($CH_{aliph.}$); 2259 (CN); 1670, 1628 (C=O)	**DMSO-d_6**, 250 MHz: 9.82 (1H, t, *J* = 5.2, NH); 8.26-8.09 (2H, m, H-5,8); 7.98-7.75 (2H, m, H-6,7); 7.66 (1H, m, H-3); 7.46 (1H, d, *J* = 7.2, H-4); 7.31 (1H, d, *J* = 8.7, H-2); 5.86 (1H, d, *J* = 5.3, OH); 4.15-3.98 (1H, m, C<u>H</u>–OH); 3.61-3.32 (2H, m, N–CH_2); 2.77 (1H, dd, J_{AX} = 4.6, *cis*-H_A CH_2–CN); 2.71 (center of AB part of ABX system, J_{AB} =16.9); 2.65 (1H, dd, J_{BX} = 6.8, *trans*-H_B CH_2–CN)

TABLE 2 (continued)

1	2	3
9b	3452 (OH); 3334 (NH); 3080 ($CH_{arom.}$); 2934 ($CH_{aliph.}$); 2251 (CN); 1668, 1641 (C=O)	**DMSO-d_6**, 100 MHz: 8.30-8.04 (2H, m, H-5,8); 7.98-7.72 (3H, m, H-4,6,7); 7.40-6.90 (3H, m, H-1,3, NH); 5.7 (1H, d, J = 5.0, OH); 4.20-3.82 (1H, m, C<u>H</u>–OH); 3.70-3.10 (2H, m, N–CH_2); 2.90-2.65 (2H, m, CH_2–CN)
10	3273 (NH); 3064 ($CH_{arom.}$); 2986, 2936, 2889 ($CH_{aliph.}$); 1675, 1636 (C=O)	**$CDCl_3$**, 300 MHz: 9.88 (1H, m, NH); 8.28 (1H, d, J = 7.2, H-8); 8.2 (1H, d, J = 7.2, H-5); 7.80-7.45 (4H, m, H-3,4,6,7); 7.08 (1H, d, J = 8.4, H-2); 4.45 (1H, m, H_X, C<u>H</u>–OH); 4.16 (1H, dd, J_{AX} = 6.0, *cis*-H_A N–CH_2); 4.00 (center of AB part of ABX system, J_{AB} = 8.4); 3.86 (1H, dd, J_{BX} = 6.3, *trans*-H_B N–CH_2). [**^{13}C NMR spectrum, $CDCl_3$**, 300 MHz: 185.10, 183.56 (C=O); 151.61; 135.24; 134.93; 134.74; 133.89; 132.96; 126.72; 117.69; 116.02; 77.42; 77.00; 76.58 (CH); 74.18 (CH<u>C</u>H_2); 67.24 (N–CH_2); 45.39 (C); 26.80, 25.30 (CH_3)]
11	3600-3100 (OH); 3280 (NH); 3070 ($CH_{arom.}$); 2919 ($CH_{aliph.}$); 1665, 1629 (C=O)	**DMSO-d_6**, 300 MHz: 9.85 (1H, t, J = 5.2, NH); 8.20 (1H, d, split, J = 7.5, J = 1.5, H-8); 8.11 (1H, d, split, J = 7.3, J = 1.5, H-5); 7.97-7.55 (3H, m, H-4,6,7); 7.42 (1H, d, J = 7.2, H-3); 7.26 (1H, d, J = 8.7, H-2); 5.08 (1H, d, J = 5.1, CH–O<u>H</u>); 4.73 (1H, t, J = 5.7, CH_2–O<u>H</u>); 3.85–3.67 (1H, m, C<u>H</u>–OH); 3.60-3.25 (2H, m, N–CH_2); 3.35-3.20 (2H, m, C<u>H</u>$_2$–OH) [**^{13}C NMR spectrum, DMSO-d_6**, 300 MHz: 183.66; 182.82; 151.55; 135.4; 134.34; 133.85; 133.24; 132.27; 126.29; 126.12; 118.66; 114.77; 111.98; 69.76 (CH_2–OH); 63.58 (CH–OH); 45.42 (N–CH_2)]
12	3448 (OH); 3270 (NH); 3070 ($CH_{arom.}$); 2919, 2857 ($CH_{aliph.}$); 1673, 1630 (C=O)	**DMSO-d_6**, 400 MHz: 9.87 and 9.83 (2H, two t, J = 5.2, NH); 8.16-7.97 (4H, m, H-5,8); 7.85-7.72 (4H, m, H-6,7); 7.58-7.52 (2H, m, H-3); 7.34 (2H, two d, J = 7.2, J = 7.6, H-4); 7.21 (2H, two d, J = 7.2, J = 7.6, H-2); 7.28-7.04 (2H, m, H-3, 5 Ph); 6.82-6.74 (2H, m, H-2, 6 Ph); 6.78-6.50 (1H, m, H-4 Ph); 5.53 и 5.40 (2H, two d, J = 4.8, J = 5.2, OH); 4.05 (2H, m, C<u>H</u>–OH); 3.80-3.26 (8H, m, NH–C<u>H</u>$_2$, N–CH_2)
13	3443 (OH); 3280 (NH); 3075 ($CH_{arom.}$); 2912 ($CH_{aliph.}$); 1663, 1627 (C=O)	**DMSO-d_6**, 400 MHz: 9.81 (2H, t, J = 5.2, NH); 8.13 (2H, d, J = 7.2, H-8); 8.04 (2H, d, J = 7.6, H-5); 7.84 (2H, dd, J = 7.2, J = 7.6, H-7); 7.77 (2H, dd, J = 7.2, J = 7.4 , H-6); 7.56 (2H, dd, J = 7.2, J = 7.6, H-3); 7.35 (2H, d, J = 7.2, H-4); 7.20 (2H, d, J = 7.6, H-2); 5.40 (2H, d, J = 4.4, OH); 3.85 (2H, m, C<u>H</u>–OH); 3.60-3.20 (4H, m, N–CH_2); 2.68-2.56 (4H, m, S–C<u>H</u>$_2$CH(OH)C<u>H</u>$_2$–S); 2.52-2.44 (4H, m, S–C<u>H</u>$_2$$CH_2$C<u>H</u>$_2$–S); 1.86-1.70 (2H, m, S–CH_2C<u>H</u>$_2$)
14	3460 (OH); 3284 (NH); 3070 ($CH_{arom.}$); 2922, 2857 ($CH_{aliph.}$); 1664, 1629 (C=O)	**DMCO-d_6**, 250 MHz, δ, ppm (J, Hz): 9.83-9.64 (2H, m, NH); 8.18-7.86 (4H, m, H-5,8); 7.70-7.50 (4H, m, H-6,7); 7.40-7.12 (7H, m, H-2,3,4 AHTP, H-2,4,5,6 1,3-disubstituted benzene); 6.84 and 6.74 (2H, two d, split, J = 8.5, J = 1.25, OH); 4.16-3.92 (2H, m, C<u>H</u>–OH); 3.57-3.02 (8H, m, C<u>H</u>$_2$CHC<u>H</u>$_2$)

form of an amorphous substance. The dimers do not have the narrow melting point range (1-2°C) characteristic of simple organic compounds. Such compounds, called molecular glasses (MG), are characterized by the vitrification temperature (vp), which is determined from the curves of differential scanning calorimetry (DSC) obtained as a result of a heating–cooling regime (10 K/min). It is seen from the data presented in Table 1 that the dimers **12** and **14** are distinguished by a more stable amorphous state, the vitrification points of which are 90 and 63°C respectively. The morphological stability of these molecular glasses is probably determined by the introduction of the flexible aliphatic chains with hydroxyl groups and chiral centers, giving rise to the formation of a diastereomeric mixture and intermolecular hydrogen bonds, and also by the comparatively high molecular mass. The elemental analyses, yields, and melting (vitrification) points are given in Table 1. The IR and ^{1}H and ^{13}C NMR spectra are given in Table 2. The results from investigation of the electrophotographic characteristics of the dimer **14** were published in [5].

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Joel FX-100 (100 MHz), Bruker AC-250 (250 MHz), Gemini-2000 (300 MHz), and Mercury-VX (400 MHz) spectrometers. The chemical shifts are given on the δ scale and were determined experimentally with reference to TMS (0 ppm) or HMDS (0.05 ppm) in $CDCl_3$, CD_3OD, or $(CD_3)_2SO_2$ (DMSO). The ^{13}C NMR spectra were recorded on a Gemini-2000 (75 MHz) or Mercury-VX (100 MHz) spectrometer. The IR spectra were recorded on Bio-Rad Digilab FTS-40 Midac PROSPECT IR and Perkin-Elmer FT-IR system Spectrum-GX spectrometers in tablets with potassium bromide. The thermal effects of the dimers were investigated on a Perkin-Elmer DSC-7 differential scanning calorimeter with heating and cooling rates of 10 K/min.

The reactions and the purity of the products were monitored by TLC on Silufol UV-254 plates with development by UV light or with iodine vapor. For column chromatography we used Silikagel (grade 62, 60-200 mesh, 150 Å) from Aldrich of Milwaukee, WI. The initial substances, catalysts, solvents, and other reagents were obtained from Reachim (Russia) or Aldrich.

1-(3-Chloro-2-hydroxypropylamino)anthraquinone (1a). In 1-chloro-2,3-epoxypropane (CEP) (296 g, 251 ml, 3.2 mol) we dissolved 1-aminoanthraquinone (40.2 g, 0.18 mol), and we added 85% acetic acid (40 ml). The mixture was stirred at 75-80°C for 25 h (TLC, eluent 1:4 acetone–hexane) and left at room temperature. The crystals that formed were filtered off, washed with 2-propanol, and dried.

2-(3-Chloro-2-hydroxypropylamino)anthraquinone (1b) and 2-[Bis(3-chloro-2-hydroxypropyl)-amino]anthraquinone (2). In CEP (296 g, 251 ml, 3.2 mol) we dissolved 2-aminoanthraquinone (40.2 g, 0.18 mol). We added 85% acetic acid (40 ml) and stirred the mixture at 75-80°C for 26 h (TLC, eluent 1:4 acetone–hexane). The mixture was left at room temperature. The crystals that formed were filtered off, washed with 2-propanol, and dried. The filtrate obtained after separation of **1b** was heated at 75-80°C until the spot of compound **1b** on the chromatogram had disappeared (about 28 h). The mixture was then treated with water to a neutral reaction, the organic layer was dried with anhydrous magnesium sulfate and filtered, and part (two thirds) of the CEP was distilled. The crystals that formed on standing were filtered off and washed with 2-propanol.

1-(2,3-Epoxypropylamino)anthraquinone (3a) and 2-(2,3-Epoxypropylamino)anthraquinone (3b). In 1,4-dioxane (200 ml) we dissolved **1a** (or **1b**) (18.9 g, 0.06 mol). We added 85% powdered potassium hydroxide (13.8 g, 0.21 mol) and stirred the mixture at room temperature for 1.5 h (2 h). At the end of the reaction (TLC, eluent 1:4 acetone–hexane) the mixture was extracted with chloroform. The organic layer was dried with anhydrous magnesium sulfate and filtered, and part (two thirds) of the solvent was distilled. The crystals that formed on standing were filtered off and washed with 2-propanol.

2-[Bis(2,3-epoxypropyl)amino]anthraquinone (4). In 1,4-dioxane (6 ml) we dissolved **2** (1 g, 2.45 mol), and we added 85% powdered potassium hydroxide (0.59 g, 9 mmol). The mixture was stirred at room temperature for 1 h (TLC, eluent 1:4 acetone–hexane). The crystals were filtered off and washed with water to a neutral reaction and then with 2-propanol.

1-(2-Hydroxy-3-piperidinopropyl)anthraquinone (5). In piperidine (8.5 g, 9.9 ml, 0.1 mol) we dissolved **1a** (3.1 g, 0.01 mol). The mixture was boiled for 4 h (TLC, eluent acetone–hexane, 1:2.6). At the end of the reaction the mixture was extracted with chloroform. The organic layer was washed several times with water to remove the excess of piperidine, dried with anhydrous magnesium sulfate, and filtered, and the chloroform was removed to dryness. The residue was dissolved by heating in 2-propanol. The crystals was filtered off, washed with cold 2-propanol, and dried.

1-(3-Diethylamino-2-hydroxypropylamino)anthraquinone (6). A mixture of **1a** (5.3 g, 0.018 mol), chloroform (20 ml), and diethylamine (13.2 g, 18.6 ml, 0.18 mol) was boiled for 7 h. At the end of the reaction (TLC, eluent acetone–hexane, 1:4) the solvent and the excess of diethylamine were distilled to dryness, and the residue was dissolved in 2-propanol. The crystals that formed on standing were filtered off, washed with 2-propanol, and dried.

1-(2-Hydroxy-3-isopropylamino)anthraquinone (7). A mixture of **1a** (5.02 g, 0.018 mol), chloroform (20 ml), and isopropylamine (10.62 g, 15.3 ml, 0.18 mol) was boiled for 7 h (TLC, eluent acetone–hexane, 1:2.6). The product was then isolated similarly to **6**.

1-[3-(Anthraquinone-1-amino)-2-hydroxypropyl]pyridinium Chlorides (8a,b). In chlorobenzene (20 ml) we dissolved **1a** (or **1b**) (9.47 g, 0.03 mol). We added pyridine (5 ml, 4.9 g, 0.062 mol) and heated the mixture at 135-140°C for 15 h (TLC, eluent acetone–hexane, 1:2.6). The crystals that formed when the reaction mixture had cooled were filtered off and washed with toluene and with hot acetone.

4-(Anthraquinone-1-amino)-3-hydroxybutanenitrile (9a) and 4-(Anthraquinone-2-amino)-3-hydroxybutanenitrile (9b). In butanone (7 ml) we dissolved **1a** (or **1b**) (5.05 g, 0.016 mol). We added potassium cyanide (1.55 g, 0.02 mol) and methanol (3 ml) and boiled the mixture at 80°C for 3 h. We then added potassium cyanide (1.55 g, 0.02 mol) and boiled the mixture for 4 h (TLC, eluent acetone–hexane, 1:4). The crystals were filtered off and washed with water and with 2-propanol.

1-(2,2-Dimethyl-1,3-dioxolane-4-methylamino)anthraquinone (10). In dry acetone (15 ml) we dissolved **3a** (2.8 g, 0.01 mol). We added three drops of $BF_3 \cdot OEt_2$ as catalyst and stirred the mixture at room temperature for 15 h. At the end of the reaction (TLC, eluent acetone–hexane, 1:4) the mixture was extracted with chloroform, the organic layer was dried with anhydrous magnesium sulfate, and the chloroform was distilled to dryness. The residue was dissolved by heating in 2-propanol. The crystals that formed on standing were filtered off, washed with cold 2-propanol, and dried.

1-(2,3-Dihydroxypropylamino)anthraquinone (11). A. In 1,4-dioxane (10 ml) we dissolved **3a** (1.7 g, 0.005 mol). We added 5% sulfuric acid (5 ml) (or 2 ml of trifluoroacetic acid) and boiled the mixture for 1 h. At the end of the reaction (TLC, eluent acetone–hexane, 1:4) the solvent was distilled to dryness, and the residue (a resin) was purified by column chromatography (eluent acetone–hexane, 1:1). A sample mixed with the compound **11** produced by method A did not give a melting point depression.

B. In butanol (8 ml) we dissolved **10** (1.35 g, 4.4 mmol). We added 85% powdered potassium hydroxide (1.05 g, 0.016 mol) and boiled the mixture for 0.5 h (TLC, eluent acetone–hexane, 1:4). The crystals that formed were filtered off, washed with 2-propanol, and dried.

N,N-Bis[1-(anthraquinone-1-amino)-2-hydroxypropyl]aniline (12). In toluene (6 ml) we dissolved **3a** (8.4 g, 0.03 mol). We added aniline (1.4 g, 0.015 mol) and heated the mixture at 135-140°C for 22 h. At the end of the reaction (TLC, eluent acetone–hexane, 1:2.6) the mixture was cooled, and the crystals that formed were filtered off, washed with 2-propanol, and dried. The product was recrystallized from a 2:1 mixture of chloroform and 2-propanol. The product was poorly soluble in traditional organic solvents (tetrahydrofuran, 1,4-dioxane, chloroform, etc.).

1,11-Di(anthraquinone-1-amino)-2,10-dihydroxy-4,8-dithiaundecane (13). In THF (30 ml) we dissolved **3a** (13.96 g, 0.05 mol). We added 1,3-propanedithiol (2.16 g, 2.39 ml, 0.02 mol) and triethylamine (0.02 mol) and stirred the mixture with boiling for 7.5 h. At the end of the reaction (TLC, eluent acetone–hexane, 1:2.6) the mixture was left in the refrigerator. The crystals that formed were filtered off and washed with 2-propanol. The product was readily soluble in chloroform, 1,4-dioxane, and THF.

Bis[3-(anthraquinone-1-amino)-2-hydroxypropylthio]benzene (14). In chloroform (50 ml) we dissolved **3a** (8.38 g, 0.03 mol). We added 1,3-benzenedithiol (1.99 g, 0.014 mol) and triethylamine (TEA) (1.63 ml) as catalyst and stirred the mixture at room temperature for 3 h. At the end of the reaction (TLC, eluent hexane–ether, 2:1) the solvent was distilled to dryness, and the residue was purified by column chromatography with 1:4 acetone–hexane as eluent. From the combined fractions with identical R_f values after removing the eluent we obtained 6.2 g (63.3%) of the resinous product **14**, a 20% solution of which was poured with vigorous stirring into a tenfold excess (by volume) of hexane. The powder that formed was filtered off, washed three times with hexane, and dried under vacuum. The product was readily soluble in chloroform, 1,4-dioxane, and THF.

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