DIOLS WITH CARBAZOLE RING AND THEIR AZA DERIVATIVES

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Abstract: Diols with carbazole ring were obtained in reactions of 9-(2- chloroethyl)carbazole with excess of diethanolamine and 9-(2,3-epoxypropyl)carbazole with water or ethylene glycol. These diols were derivatized into aza compounds by the reactions with aromatic diazaamines. The compounds were isolated and characterized by elemental analysis, IR, UV-VIS and ^{1}H NMR spectroscopy. The obtained compounds are precursor of polyetherols with carbazole ring, which can be obtained in straightforward reaction with ethylene or propylene oxides.

Introduction

Introduction of some azacyclic rings, like 1,3,5-triazine, perhydrotriazine or purine into polymers, for instance polyurethanes or polyesters enhances their thermal stability [1-3]. Substrates for synthesis of those polymers are polyetherols containing azacyclic rings which can be obtained from isocyanuric acid, melamine, uric acid or their derivatives with oxiranes used in excess.

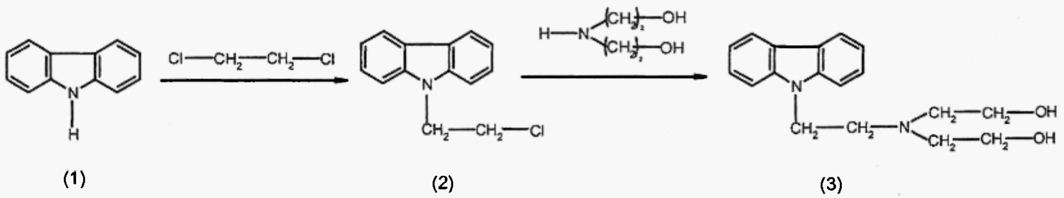
Carbazole is thermally stable. It decomposes upon heating starting at 320^{0}C. The polymers with carbazole ring included in their structure have some unique physical properties; they are photo- and electroluminescent, often are liquid crystals and posses electroconductivity and and non-linear optical properties [4-10]. The presence of aza groups in carbazole enhances these valuable properties [11]. Synthesis of bi-functional polyetherols with carbazole ring was not reported till now. Probably the reason was mono-functionality of carbazole and its low solubility precluding the control of its reaction with oxiranes.

We aimed at modification of carbazole in order to obtain low-molecular weight diols, soluble in oxiranes and reacting with them to give bi-functional polyetherols. Moreover the presence of aza groups in diols could lead to semiproducts applicable for synthesis of new polymers of non-linear optical properties. Therefore the aza groups were introduced straight into carbazole ring.

Results and Discussions

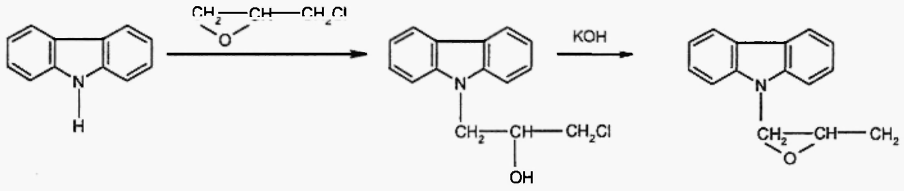
Diols with carbazole ring were obtained via two independent routes:

The first method was based on reaction of carbazole **1** with ethylene chloride, then the 9-(2-chloroethyl)carbazole **2** was treated with diethanolamine:



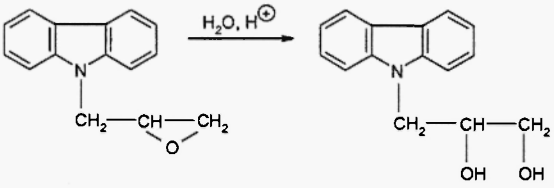
First step was preformed in neat 1,2-dichloroethane, in presence of K_2CO_3 and [Bu$_4$N]I as phase transfer catalyst according to described protocol [12]. The crude product was crystallized from ethanol (m.p. 124 – 126°C). The diol **3** was obtained from **2** with excess of diethanolamine in presence of K_2CO_3 in order to neutralize HCl evolved.

The second synthetic procedure involved addition of glycerine epichlorohydrine (ECH) to **1** to give initially 9-(2,3-epoxypropyl)carbazole **5** in the reaction:



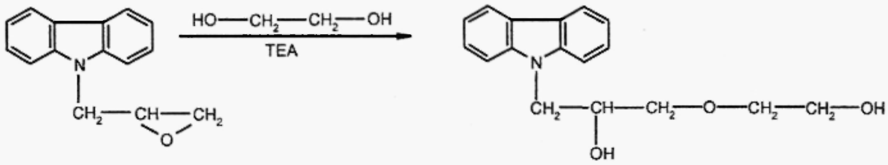
(4) (5)

Ring opening of **5** with water in acidic conditions led to **6**:



(6)

or **7** when ethylene glycol in presence of triethylamine (TEA) catalyst was used:



(7)

Epoxidation of carbazole was performed at 50 - 56°C in acetone with six-fold excess of ECH and two-fold molar excess of KOH [13]. Crude product **5** was obtained as oil, which was dissolved in acetone, poured onto water, pH was adjusted to about 1 with sulfuric acid and the product was obtained as creamy solid. Diols **6** and **7** were then coupled with diaza amines: 2-chloro-4-nitroaniline, 2,4-chloro-2-nitroaniline, 2,4-dinitroaniline and 6-chloro-2,4-dinitroaniline.

The amines less active than 2-chloro-4-nitroaniline were proven not to react with carbazole [14]. Diazotization was performed by two different method. In the first one 2-chloro-4-nitroaniline was reacted with sodium nitrite and concentrated hydrochloric acid at temperature below 5^0C. Diaza chloride was not isolated; instead the diol suspended in isopropyl alcohol was added into this solution. Vigorous stirring of heterogeneous reaction mixture was necessary at this stage due to limited miscibility of isopropyl alcohol with water.

Other amines did not undergo facile diazotization in the above conditions. Therefore nitrozosulfuric acid was used for diazotization, and diols were added into diaza salts in situ in analogous manner as in previous case except lower temperature was used (15^0C in comparison with 40^0C in method 1) for shorter time (1 hour in comparison with 24 in method 1). It should be noticed here that diols were coupled into aza dyes of orange to red colour except 6-(carbazol-9-yl)-3-oxahexane-1,5-diol, which upon reaction with diazotized 4-chloro-2-nitoaniline, 2,4-dinitroaniline and 6-chloro-2,4-dinitroaniline resulted in formation of resin products.

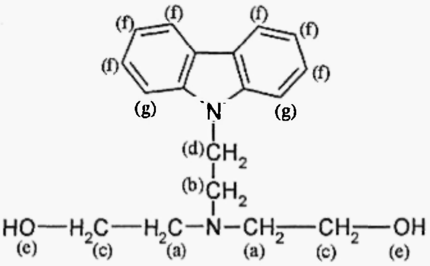
IR spectra of diols showed characteristic valence and deformation mode bands of –OH groups within the 3360-3400 cm^{-1} and 1120-1060 cm^{-1}, respectively. Also the carbazole ring skeleton bands were observed at 1626, 1451, 1327, 1010-928 cm^{-1}. The aza derivatives showed the N=N stretching bands within the 1594-1606 cm^{-1} region. UV-Vis spectra of those derivatives contain the absorption bands in the 430 – 450 nm region. The ^{1}H-NMR spectra are composed of aromatic proton resonances at 7.0-9.0 ppm and –OH resonance at 2.7-4,9 ppm (see Experimental). All diols were well soluble in oxiranes: ethylene and propylene oxides and in epichlorhydrine upon heating to *ca* 40°C. In presence of TEA catalyst the addition of oxirane to semiproduct took place. Thus, when temperature of the mixture was elevated to and maintained within 60 - 90°C for about 56 hours, the polyetherols terminated with free hydroxyl groups at one and carbazole at the opposite one could be obtained.

Experimental

Reaction of 9-(2-chloroethyl)carbazole with diethanolamine

In the three-necked, round-bottomed of 250 cm^3 capacity, equipped with reflux condenser, mechanical stirrer, and thermometer 23 g (0.076 mole) of 9-(2-chloroethyl)carbazole and 76 g (0.76 mola) of diethanolamine (DEA) were placed. 9-(2-Chloroethyl)carbazole was dissolved in DEA at 105 - 110°C temperature. Then 8.4 g of Na_2CO_3 (0.076 mole) was added. Two mixtures were combined and heated at 115 ÷ 120°C for 10 hrs. Then the mixture was poured into 1500 cm^3 water. The precipitate was formed, filtered off on Büchner funnel, dried in vacuo at 35°C.

3-[2-(Carbazol-9-yl)ethyl]-3-azapentane-1,5-diol

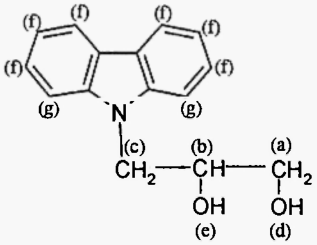


Yield - 74 %; m.p. 53-55.5^{0}C; elemental analysis - % Calcd.: C 72,43; H 7,38; N 9,39; % Found.: C 72,23; H 7,10; N 9,17; IR (KBr), [cm^{-1}]: 3914, 3277 (O-H), 3050 (Ar-H), 2944, 2923, 2877, 2841 (CH_2) 1626-1458 (C=C), 1458 (CH_2) 1335 (C-N), 1237, 1206, 1151, 1072, 1048, 1041 (C-O), 748,725 (Ar-H); ^{1}H-NMR (d_6-DMSO-), [ppm]: (a) 2,7 t; (b) 2,9 t; (c) 3,4 t; (d) 4,5 t; (e) 5,9 s; (f) 7,0-7,7 m; (g) 8,0-8,3 d.

Epoxide ring opening with water

In the three-necked, round-bottomed of 250 cm^3 capacity, equipped with reflux condenser, mechanical stirrer, and thermometer 5 g (0.02 mole) of 9–(2,3–epoxypropyl)carbazole obtained as before and 50 cm^3 acetone were placed. The mixture was heated until it became homogenous at 50 – 68°C. Then 70 cm^3 of water was added and pH was adjusted to 1 with 50% sulfuric acid. The reaction was monitored by determination of epoxide number. After reaction was completed the mixture was poured into 3 dm^3 of water which immediately gave pale-pink precipitate. The product 3-(carbazol-9-yl)propane-1,2-diol was filtered off and vacuum dried at 90 - 100°C.

3-(9-Carbazolyl)propane-1,2-diol

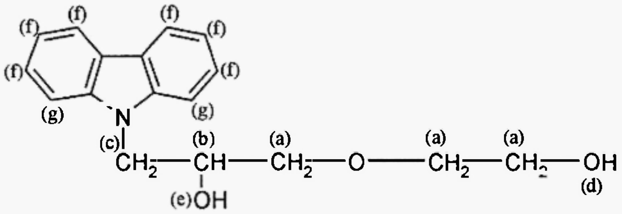


Yield – 75,3 %; m.p. 131-132.8^{0}C; elemental analysis - % Calcd.: C 74,62; H 6,22; N 5,80; % Found.: C 74,74; H 6,27; N 5,73; IR (KBr) [cm^{-1}]: 3360 (O-H) 3050 (Ar-H) 2969, 2934, 2909, 2875 (CH_2), 1629-1461 (C=C), 1454 (CH_2, OH), 1370, 1355, 1256 (CH_2), 1328 (C-N), 1048, 1032, 1022 (C-O), 747, 724 (Ar-H); ^{1}H-NMR (d_6-DMSO-), [ppm]: (a) 3,4 t; (b) 3,9 s; (c) 4,4 2d; (d) 4,9 s; (e) 5.0 d; (f) 7,1-7,9 m; (g) 8,0-8,3 d.

Epoxide ring opening with ethylene glycol

In the three-necked, round-bottomed flask of 250 cm^3 capacity, equipped with reflux condenser, mechanical stirrer, and thermometer 45 g (0.18 mole) of 9–(2,3–epoxypropyl)carbazole and 76.5 cm^3 dioxane were placed. The mixture was stirred at 50°C until epoxide had dissolved. Then 13.5 g (0.18 mole) of ethylene glycol and 4.5 cm^3 TEA were added. Temperature was raised into 110 – 118°C and mixture was heated until completion of reaction, which was determined on the basis of determination of epoxide number. Dioxane was removed from the mixture by vacuum distillation. The product slowly crystallized from this mixture.

6-(9-Carbazolyl)-3-oxahexane-1,5-diol



Yield – 74%; m.p. 45.5-47^{0}C; elemental analysis - % Calcd.: C 71,53; H 6,66; N 4,91; % Found.: C 71,80; H 6,47; N 5,01; IR (KBr) [cm^{-1}]: 3342 (O-H), 3048, 3022 (Ar-H), 2927, 2870 (CH_2), 1627-1460 (C=C), 1460-1452 (CH_2, OH), 1349, 1335 (CH_2), 1326 (C-N), 1154, 1030 (C-O), 1129, 1121 (C-O in sec. alc.), 1029,1061 (C-O in prim. alc.) 750, 723 (Ar-H); ^{1}H-NMR (d_6-DMSO-), [ppm]: (a) 3,2-3,7; (b) 3,9-4,2; (c) 4,2-4,6; (d) 4,6-4,7; (e) 5,0-5,1; (f) 7,0-7,8; (g) 8,0-8,3.

Synthesis of diaza dyes

Diazotization of 2-chloro-4-nitroaniline

In a 100 cm^3 beaker 2.588 g (0.015 mole) of 2-chloro-4-nitroaniline or 2.588 g (0.015 mole) 4-chloro-2-nitroaniline was dispersed in 32.4 cm^3 water. To this suspension 10.2 cm^3 of concentrated hydrochloric acid (in case of 2-chloro-4-nitroaniline). The mixture was cooled down to below 5°C. The solution of 1.034 g (0.015 mole) of sodium nitrite in 744 cm^3 water was added in small portions. The solution of diaza salt was further stirred in 0-5°C for next 30 minutes.

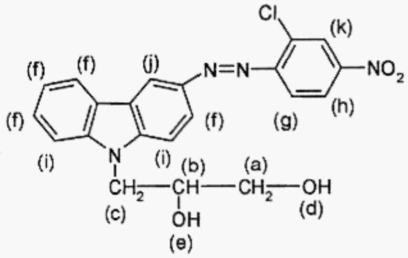
Diazotization of 4-chloro-2-nitroaniline, 2,4-dinitroaniline and 6-chloro-2,4-dinitroaniline

In a three-necked flask equipped with mechanical stirrer, thermometer and reflux condenser 0.984 g (0.014 mola) of sodium nitrite in 2 cm^3 of concentrated sulfuric acid (d = 1.841 g/cm^3) was placed. The mixture was heated up to 70°C in oil bath and stirred for one hour, then cooled to 15°C and the solution of 0.012 mole of amine (2.071 g of 4-chloro-2-nitroaniline, 2.197 g of 2,4-dinitroaniline or 2.61 g of 6-chloro-2,4-dinitroaniline) in 10.5 cm^3 of acetic acid was added. The mixture was stirred at this temperature for one hour.

Coupling of diols with diaza salt of 2-chloro-4-nitroaniline

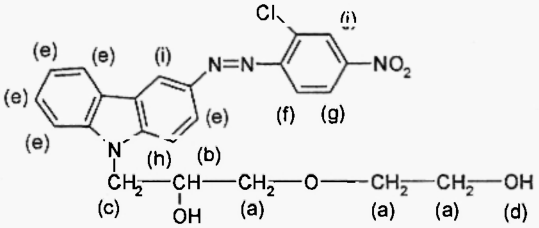
In a three-necked flask equipped with mechanical stirrer, thermometer and reflux condenser 2.89 g of 3-(carbazol-9-yl)propane-1,2-diol or 3.42 g of 6-(carbazol-9-yl)-3-oxahexane-1,5-diol (0.012 mole) dissolved in 20 cm^3 isobutyl alcohol was placed. This suspension was heated to 40°C, and then to this mixture the solution of diaza salt of 2-chloro-4-nitroaniline was added dropwise within one hour. The mixture was stirred for the next 24 hours, the product was precipitated, which was filtered off, washed with small amount of isobutyl alcohol, then with water until filtrate was neutral. The product was crystallized from 1,2-dichloroethane.

3-[3-(2-Chloro-4-nitrophenylazo)carbazol-9-yl]propane-1,2-diol



Yield – 35%; m.p. 203-205^{0}C; elemental analysis - % Calcd.: C 59,36; H 4,03; N 13,19; % Found.: C 59,11; H 4,16; N 12,95; IR (KBr) [cm^{-1}]: 3397 (O-H), 3097, 3087 (Ar-H), 2933-2879 (CH_2), 1626-1465 (C=C), 1595 (N=N), 1521, 1340 (NO_2), 1341 (C-N), 1111 (C-Cl), 1045 (C-O), 744 (Ar-H); ^{1}H-NMR (d_6-DMSO-), [ppm]: (a) 3,40 t, J = 7 Hz; (b) 3,90 m, J = 7 Hz; (c) 4,40 d, J = 7 Hz; (d) 4,85 t, J = 7 Hz; (e) 5,00 d, J = 7 Hz; (f) 7,10-7,90 m; (g) 7,70 d, J = 9 Hz; (h) 8,05 dd, J_1 =9 Hz, J_2 = 2 Hz; (i) 8,10-8,30 m; (j) 8,40 d, J = 2 Hz; (k) 8,75 d, J = 2 Hz; UV (CH_3OH), [nm]: λ_{max} = 444, 4.

6-[3-(2-Chloro-4-nitrophenylazo)carbazol-9-yl]-3-oxahexane-1,5-diol



Yield – 22% , m.p. 88-90^{0}C; elemental analysis - % Calcd.: C 58,96; H 4,52; N 11,97; % Found.: C 58,67; H 4,53; N 12,24; IR (KBr) [cm^{-1}]: 3341 (O-H), 3097, 3053 (Ar-H), 2921, 2875 (CH_2), 1626-1464 (C=C), 1595 (N=N), 1519, 1341 (NO_2), 1464-1452 (CH_2, OH), 1341 (C-N), 1164 (C-O in ethers), 1120 (C-O), 1120 (C-Cl), 1060-1046 (C-O in primary alcohols), 745 (Ar-H); ^{1}H-NMR (d_6-DMSO-),

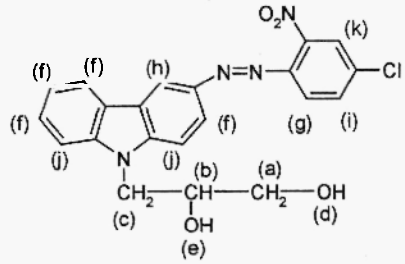
[ppm]: (a) 3,00-3,75 m; (b) 3,75-4,20 m; (c) 4,20-4,70 m; (d) , br. s, overlapped with (b) and (c); (e) 7,10-7,90 m; (f) 7,75 d, $J_1 = 9$ Hz; (g) 7,70 d, J = 9 Hz; (h) 8,15 dd, $J_1 = 9$ Hz, $J_2 = 2$ Hz; (i) 8,45 d, J = 2 Hz; (j) 8,80 d, J = 2 Hz; UV (CH_3OH), [nm]: $\lambda_{max} = 443$.

Coupling of diols with diaza salts of 4-chloro-2-nitroaniline, 2,4-dinitroaniline or 6-chloro-2,4-dinitroaniline

In a three-necked flask equipped with mechanical stirre , thermometer and reflux condenser the suspension of 2.89 g of 3-(9-carbazolyl)propane-1,2-diol or 3.42 g of 6-(carbazol-9-yl)-3-oxahexane-1,5-diol (0.012 mole) and 18 cm^3 isobutyl alcohol and 5 cm^3 water was placed. To this mixture the solution of diaza salt of 4-chloro-2-nitroaniline, 2,4-dinitroaniline or 6-chloro-2,4-dinitroaniline was adeed dropwise. The mixture was stirred for one hour, the precipitate was formed, which was filtered off, washed with small amount of isobutyl alcohol, then with water until filtrate was neutral. The product waqs crystallized from 1,2-dichloroethane.

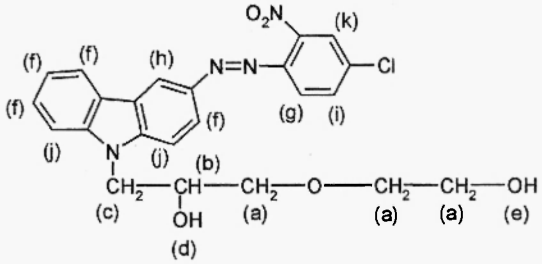
Remark : In the coupling reactions described above the 25% molar excess of amine was used.

3-[3-(4-Chloro-2-nitrophenylazo)carbazol-9-yl]propane-1,2-diol



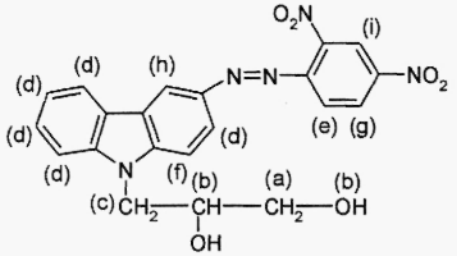
Yield – 38%, m.p. 95-98°C; elemental analysis - % Calcd.: C 59,42; H 4,04; N 13,21; % Found.: C 59,12; H 4,02; N 12,95; IR (KBr) [cm^{-1}]: 3389 (O-H), 1627-1466 (C=C), 1597 (N=N), 1533, 1261 (NO_2), 1358, 1261 (C-N), 1104 (C-Cl), 801 (Ar-H); ^{1}H-NMR (d_6-DMSO-), [ppm]: (a) 3,40 t, J = 7 Hz; (b) 3,85 m; (c) 4,40 t, J = 7 Hz; (d) 4,80 t J = 7 Hz; (e) 5,00 d, J = 7 Hz; (f) 7,10-7,70 m; (g) 7,20 d; (h) 7,70-8,05 m; (i) 7,80-8,00 m; (j) 8,15-8,35 m; (k) 8,70d, J = 2 Hz; UV (CH_3OH), [nm]: $\lambda_{max} = 417, 6$.

6-[3-(4-Chloro-2-nitrophenylazo)carbazol-9-yl]-3-oxahexane-1,5-diol



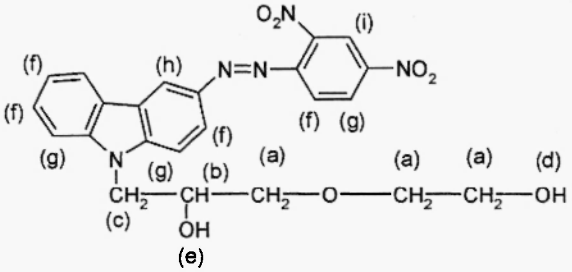
Yield – 28%, elemental analysis - % Calcd.: C 58,91; H 4,51; N 11,95; % Found.: C 58,28; H 4,46; N 12,01; IR (KBr) [cm^{-1}]: 3379 (O-H), 3049, 3025 (Ar-H), 2956-2870 (CH_2), 1626-1482 (C=C), 1594 (N=N), 1530, 1334 (NO_2), 1459, 1452 (CH_2, OH), 1324 (C-N), 1153 (C-N), 1128 (C-O in prim. alc.), 1120 (C-Cl), 1049, 1020 (C-O in prim. alc.), 747-722 (Ar-H); ^{1}H-NMR (d_6-DMSO-), [ppm]: (a) 3,00-3,70 m; (b) 3,80-4,20 m; (c) 4,20-4,50 m; (d) 4,60 s; (e) 5,10 s; (f) 6,90-7,95 m; (g) 6,90-7,15 m; (h) 7,70-7,95 m; (i),(j) 7,95-8,35 m; (k) 8,70 d, J= 2 Hz.; UV (CH_3OH), [nm]: $\lambda_{max} = 414$.

3-[3-(2,4-Dinitrophenylazo)carbazol-9-yl]propane-1,2-diol



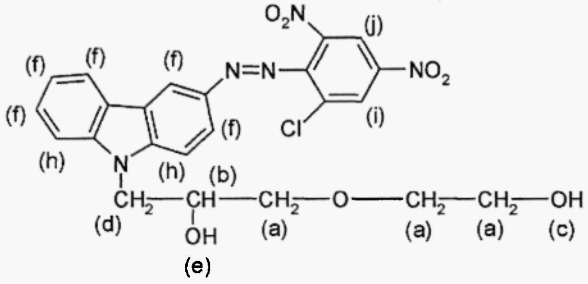
Yield – 18% , m.p. 200-202^{0}C; elemental analysis - % Calcd.: C 57,93; H 3,94; N 16,09; % Found.: C 57,67; H 3,84; N 15,93; IR (KBr) [cm^{-1}]: 3245 (O-H), 3095-3047 (Ar-H), 1626-1481 (C=C), 1593 (N=N), 1526, 1339 (NO$_2$), 1464-1430 (CH$_2$, OH), 1339 (C-N), 1060-1020 (C-O in prim. alc.), 742 (Ar-H); ^{1}H-NMR (d$_6$-DMSO-), [ppm]: (a) 3,30 d, J = 7 Hz; (b) 3,50-4,20 m; (c) 3,50, J = 7 Hz; (d) 7,10-7,80 m; (e) 7,85 d, J = 9 Hz; (f) 8,25 d, J = 9 Hz; (g) 8,55 dd; J$_1$ = 9 Hz, J$_2$ = 2 Hz; (h) 8,75 d, J = 2 Hz; (i) 8,85 d, J = 2 Hz; UV (CH$_3$OH), [nm]: λ_{max} = 449.

6-[3-(2,4-Dinitrophenylazo)carbazol-9-yl]- 3-oxahexane-1,5-diol



Yield – 45%; elemental analysis - % Calcd.: C 57,61; H 4,41;N 14,61; % Found.: C 57,76; H 4,46; N 14,76; IR (KBr) [cm^{-1}]: 3332 (O-H), 3100-3052 (Ar-H), 2959-2872 (CH$_2$), 1626-1483 (C=C), 1589 (N=N), 1522, 1324 (NO$_2$), 1459-1452 (CH$_2$, OH), 1324 (C-N), 1154 (C-O in ethers), 1129 (C-O in sec. alc.) 1011-1020 (C-O in prim. alc.), 750-710 (Ar-H); ^{1}H-NMR (d$_6$-DMSO-), [ppm]: (a) 3,20-3,70 m; (b) 3,90-4,20 m; (c) 4,20-4,60 m; (d) 4,40-4,70 m; (e) 4,90-5,20 m; (f) 7,00-7,75 m; (g) 7,75-8,45 m; (h) 8,50-8,70 m; (i) 8,70-8,95 m; UV, (CH$_3$OH), [nm]: λ_{max} = 448.

6-[3-(2-Chloro-4,6-dinitrophenylazo)carbazol-9-yl]-3-oxahexane-1,5-diol



Yield –36 %, elemental analysis - % Calcd.: C 53,75; H 3,92;N 13,63; % Found.: C 53,80; H 3,62; N 13,45; IR (KBr) [cm^{-1}]: 3359 (O-H), 3092, 3057 (Ar-H), 2960, 2931, 2872 (CH$_2$), 1617-1483 (C=C), 1593 (N=N), 1537, 1335 (NO_2), 1459, 1452 (CH_2, OH), 1324 (C-N), 1154 (C-O in ethers) 1117 (C-Cl), 1070-1021 (C-O in primary alc.), 750-722 (Ar-H); ^{1}H-NMR (d_6-DMSO-), [ppm]: (a) 3,30-3,75 m; (b) 3,80-4,20 m; (c) 3,80-4,20 s (b and c signals overlap); (d) 4,20-4,60 m; (e) 4,20-4,60 s (d and e signals overlap); (f) 6,90-7,90 m; (g) 6,90-7,15 m; (h) 7,90-8,50 m; (i) 8,45 d, J = 2 Hz; (j) 8,60-8,80 m, UV (CH_3OH), [nm]: $\lambda_{max} = 381$.

Analyses

Epoxy number in the course of epoxide ring opening procedure was monitored by hydrochloric method in dioxane [15]. The ^{1}H NMR spectra were recorded with Brucker AMX300 spectrometer, IR spectra were taken with the use of Perkin Elmer (PARAGON 1000 FT) spectrophotometer. Elemental analyses were performed with EA 1108 (Carlo-Erba) analyzer. UV/VIS spectra were obtained with BECKMAN DU-640 spectrophotometer in methanol.

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