Synthesis of a bifunctional 1,2,3,4-tetrahydroquinoline derivative: 1,8-bis(9-ethyl-9*H*-carbazol-3-yl)-1,2,3,4,5,6,7,8-octahydro-quino[5,6-*f*]quinoline-3,6-diol

Rimgaile Degutyte, Maryte Daskeviciene, Jolanta Stumbraite, and Vytautas Getautis*

Department of Organic Chemistry, Kaunas University of Technology, Radvilenu pl. 19, LT-50279 Kaunas, Lithuania
E-mail: vgetaut@ktu.lt

Abstract
N,N`*-Di(3-chloro-2-hydroxypropyl)-*N,N`-di(9-ethyl-9*H*-carbazolyl)-2,7-diaminonaphthalene upon intramolecular cyclization gives 1,8-bis(9-ethyl-9*H*-carbazol-3-yl)-1,2,3,4,5,6,7,8-octahydroquino[5,6-*f*]quinoline-3,6-diol.

Keywords: 1,2,3,4-Tetrahydroquinoline; epichlorohydrin; regioselective cyclization; 1,8-bis(9-ethyl-9*H*-carbazol-3-yl)-1,2,3,4,5,6,7,8-octahydroquino[5,6-*f*]quinoline-3,6-diol

Introduction

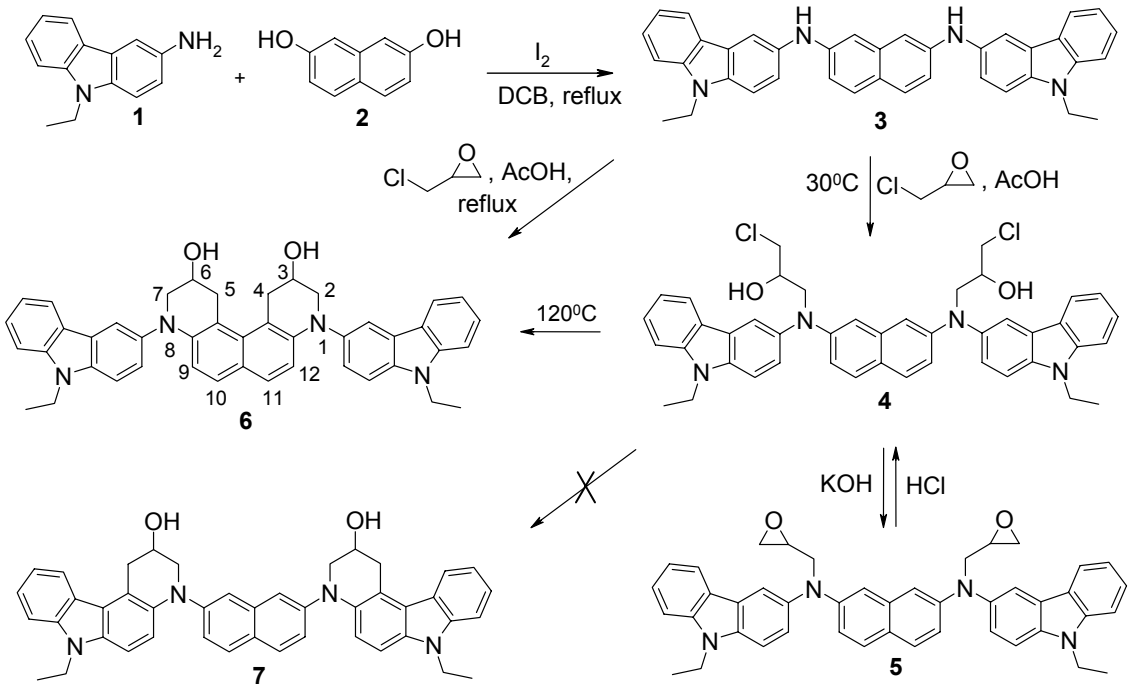
During recent years rapid developments in the chemistry of 1,2,3,4-tetrahydroquinolines have been observed[1]. The growing interest in them can be explained by their biological activities. Substituted tetrahydroquinolines are the core structures in many important pharmacological agents[2-6], many relatively simple synthetic 1,2,3,4-tetrahydroquinolines are already in use or have been tested as potential drugs.[7-9] Besides pharmaceutical applications, tetrahydroquinoline derivatives are useful as pesticides[10], antioxidants[11], corrosion inhibitors[12], and active components of various dyes[13]. In addition, they also have found application in modern recording technologies.[14,15] On the other hand, the carbazole core is present in the structure of some alkaloids[16-18], also it is known to be included in semiconductor properties exhibiting compounds which are used in various optoelectronic applications.[19,20]

Here we targeted our efforts to develop a synthesis method of bifunctional 1,2,3,4-tetrahydroquinoline derivative possessing 9-ethylsubstituted carbazolyl radicals that could be a promising synthon for synthesis of new biological or electroactive compounds.

Results and Discussion

In our previous works we developed a synthetic methodology for the synthesis of a bifunctional tetrahydroquinoline core starting from a symmetrical diphenylamine, which was successively reacted with epichlorohydrin, followed by ring opening of the epoxypropyl derivative to a 3-chloro-2-hydroxypropyl substituted compound, that was finally cyclized in a regioselective fashion to a bifunctional condensed tetrahydroquinoline derivative.[21,22]

This prompted us to apply these procedures for the instant pathway, starting from *N,N*'-di(9-ethyl-9*H*-carbazolyl)-2,7-diaminonaphthalene (**3**), which was prepared by iodine-catalysed condensation of 2,7-dihydroxynaphthalene with 3-amino-9-ethylcarbazole (Scheme 1).



Scheme 1

Surprisingly, we failed to form the expected epoxy compound **5** from **3** by the action with epichlorohydrin under alkaline conditions. Therefore, it lead to an attempt to synthesize *N,N`*-di(3-chloro-2-hydroxypropyl)-*N,N`*-di(9-ethyl-9*H*-carbazolyl)-2,7-diaminonaphthalene (**4**) from **3** by alkylation with epichlorohydrin in the presence of acetic acid as catalyst in refluxing methanol. The desired product could not be isolated either, because of the complexity of the reaction mixture. The lowering of the reaction temperature to 30°C gave a result – two products during TLC monitoring, one of them (presumably monofunctional) gradually blending in favour of the other. An attempt to convert the product to easily crystallizable epoxy derivative **5** by the work-up with KOH was successful, thus proving the initial structure of **4**. Reconverting of **5** to **4** upon the action of HCl, and especially trying to purify it by flash chromatography gave the

conclusion about the instability of chloropropyl derivative **4** towards intramolecular cyclization already in the column. Thus, by means of mass spectra, a monocyclic tetrahydroquinoline derivative was detected ($[M+H]^+$=693) among the eluted products. Then, the crude compound **4** was attempted to further reaction by refluxing it in epichlorohydrin (the latter was used to neutralize the liberating HCl), and the reaction was completed in 3 hours to give a target dicyclic product **6**.

The structures of isolated intermediates **4** and **5** were proved by spectral data, what confirmed the expected course of the reaction.

Since we could expect two possible sites of electrophilic attack of the aliphatic side chains in **4**, and consequently two presumable tetrahydroquinoline products (**6** or **7**), the actual structure was resolved from the spectral data.

Thus, the mass spectrum and elemental analysis data are consistent with both probable structures **6** or **7**. In the ^{1}H NMR spectrum (*DMSO*-d_6, CS_2) of the isolated product signals are present which can be assumed to the five non-equivalent protons of the formed tetrahydroquinoline ring. The OH proton gives a sharp doublet at 5.17 ppm and a doublet of the same intensity at 4.96 ppm, as this group is attached to stereogenic centre; this indicates formation of two diastereomers, what is evidenced by a double set of signals of other neighbouring groups. The preservation of a hydroxyl is confirmed also by an absorption band at 3273 cm^{-1} in the IR spectrum.

A consideration of two-dimensional ^{1}H-^{1}H COSY data facilitated the assignment of resonances to appropriate heteroaromatic protons (Fig. 1). The 5`-H proton of carbazole with the largest chemical shift 8.06 ppm appears as a doublet ($J$ = 7.8 Hz) and exhibits a clear correlation with two doublets upfield (at 7.16, 7.14 ppm ($J$ = 7.8 Hz), which can be assumed to 6`-H, due to vicinal coupling with 5`-H and 7`-H. A doublet at 7.09 ppm (J = 8.9 Hz) was attributed to 11-H and 10-H of naphthalene core because of clear correlation with a doublet of 12-H and 9-H of naphthalene moiety (6.49 ppm, J = 8.9 Hz).

The direction of the intramolecular cyclization can be estimated from the analysis of aromatic part of ^{1}H NMR spectrum of the cyclized product (Fig. 2). The preservation of a signal at 7.99 ppm of 4`-H of carbazole, splitted to a doublet due to coupling with 2`-H (J = 2.1 Hz), and in addition, the disappearance of a characteristic doublet in the region 6.98-6.90 ppm (J = 1.9-2.4 Hz), which was observed in the spectra of compounds **3**, **4** and **5**, (and had been attributed to 1-H and 8-H of naphthalene) favours definitely structure **6** from the two. Moreover, the substitution of 1-H (and 8-H analogously) in naphthalene can be clearly confirmed from the data of the appropriate part of ^{1}H NMR data. The resonance of 3-H in compounds **3, 4** and **5** gives rise to doublet of doublets due to its vicinal coupling to the 4-H (J = 8.7, 8.9 and 8.9 Hz, respectively) and coupling to 1-H (J = 1.9, 2.1 and 2.4 Hz). In the cyclization product the corresponding proton gives only a doublet (J = 8.9 Hz) because of missing of a *meta*-proton, a characteristic fact for structure **6**.

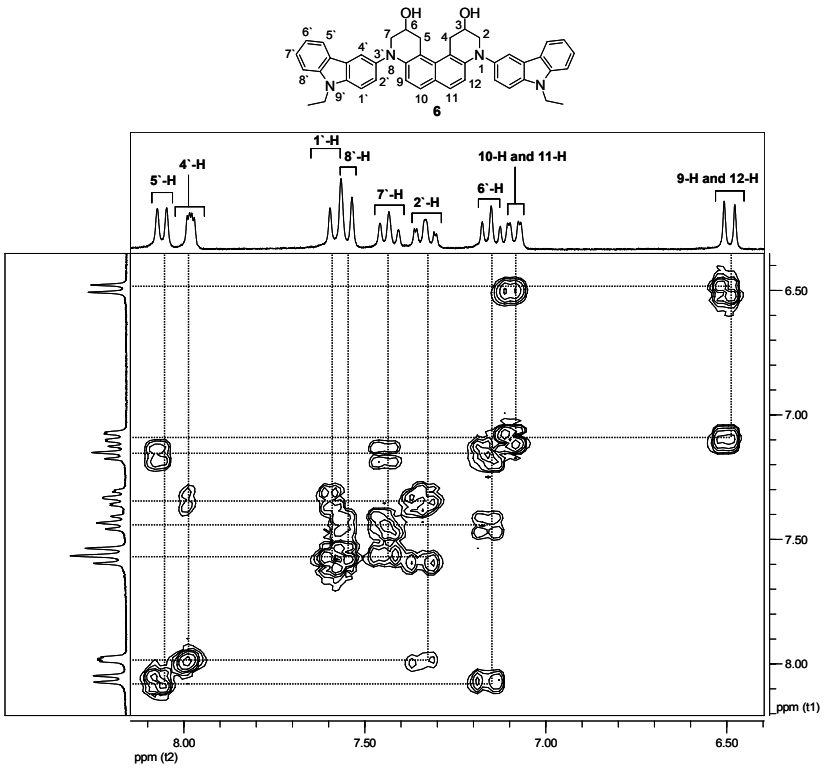


Figure 1. Aromatic part of 2D ^{1}H-^{1}H-COSY-NMR spectrum of **6** in *DMSO*-d_6 and CS_2

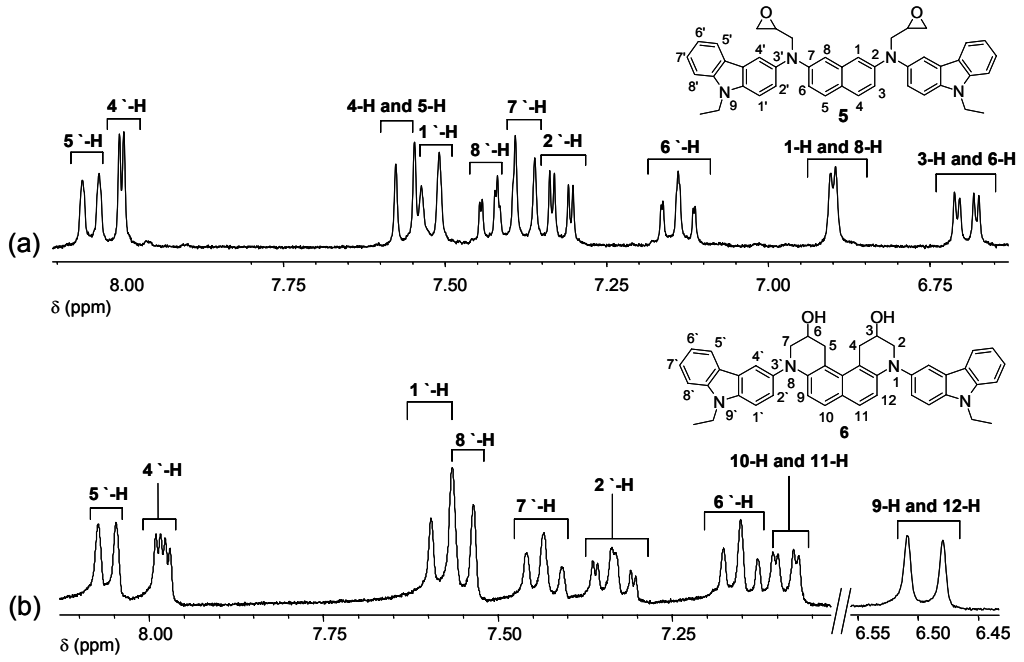


Figure 2. (a) Aromatic part of the ^{1}H NMR spectrum of **5** (300 MHz, $CDCl_3$, *DMSO*-d_6), (b) aromatic part of the ^{1}H NMR spectrum of **6** (300 MHz, *DMSO*-d_6, CS_2)

From all this we can conclude unambiguously, that cyclization occurs at 1- and 8-position of the naphthalene ring to give one of the presumable bifunctional compounds - 1,8-bis-(9-ethyl-9*H*-carbazol-3-yl)-1,2,3,4,5,6,7,8-octahydroquino[5,6-*f*]quinoline-3,6-diol (**6**).

Finally, while seeking for optimal conditions, we supposed the possibility for the synthesis of **6** by one-pot reaction from **3**; the methodology developed requires 25h reflux of *N*,*N*'-di(9-ethyl-9*H*-carbazolyl)-2,7-diaminonaphthalene (**3**) in epichlorohydrin in the presence of 85% acetic acid.

Conclusions

In conclusion, a one-pot synthesis of 1,8-bis(9-ethyl-9*H*-carbazol-3-yl)-1,2,3,4,5,6,7,8-octahydroquino[5,6-*f*]quinoline-3,6-diol has been developed starting from ,*N*'-di(9-ethyl-9*H*-carbazolyl)-2,7-diaminonaphthalene by alkylation with epichlorohydrin and following intramolecular cyclization.

Experimental Section

General Procedures. The NMR spectra were taken on a Varian Unity Inova spectrometer (300 MHz for ^{1}H and 75 Hz for ^{13}C). The IR spectra were taken for samples in KBr pellets on a Perkin Elmer Spectrum BX II FT-IR System spectrometer. Mass spectra were recorded on Waters (Micromass) 2Q 200. Melting points were determined in capillary tubes on capillary melting point apparatus MEL-TEMP. The course of the reactions was monitored by TLC on Silufol UV-254 plates (acetone/*n*-hexane = 1/3), which were developed with I_2 or UV light. Silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) was used for column chromatography. Elemental analyses were performed with an Exeter Analytical CE-440 Elemental Analyzer; their results agreed satisfactorily with the calculated values.
3-amino-9-ethylcarbazole (90 %) was purchased from Sigma-Aldrich and used without further purification.

***N*,*N*'-Di(9-ethyl-9*H*-carbazolyl)-2,7-diaminonaphthalene (3)**
A mixture of 3-amino-9*H*-ethylcarbazole (**1**) (25 g, 0.1 mol), 2,7-dihydroxynaphthalene (**2**) (7.9 g, 50 mmol), I_2 (0.4 g) (68 mL) was refluxed in 68 mL of 1,2-dichlorobenzene (DCB) for 5 h. After termination of the reaction, to a reaction mixture methanol (170 mL) was added and upon cooling a crystalline product formed. The crystals were filtered off, washed with diethyl ether and recrystallized from toluene to yield **3** (20 g, 62%), mp 232-234.5°C; IR (KBr, cm^{-1}) 3392 (NH), 3049 (CH_{arom}), 2975, 2932, 2886 (CH_{aliph}), 1625, 1577 (C=C), 1226, 1193 (C-N), 860, 742 ($CH{=}CH_{arom}$); ^{1}H NMR (300 MHz, $CDCl_3$, *DMSO*-d_6, ppm) δ 8.15 (2H, s, NH), 8.01 (2H, d, J = 7.5 Hz, 5-H of carbazole), 7.89 (2H, d, J = 1.8 Hz, 4-H of carbazole), 7.49 (2H, d, J = 8.7 Hz, 4-

H and 5-H of naphthalene), 7.44 (4H, d, *J* = 8.7 Hz, 1-H, 8-H of carbazole), 7.38, 7.36 (2H, two dd, *J* = 7.5, 8.7, 1.2 Hz, 7-H of carbazole), 7.32 (2H, dd, *J* = 8.7, 1.8 Hz, 2-H of carbazole), 7.11, 7.08 (2H, two dd, *J* = 7.5, 0.9 Hz, 6-H of carbazole), 6.98 (2H, d, *J* = 1.9 Hz, 1-H and 8-H of naphthalene), 6.94 (2H, dd, *J* = 8.7, 1.9 Hz, 3-H and 6-H of naphthalene), 4.36 (4H, q, *J* = 7.2 Hz, CH_2), 1.34 (6H, t, *J* = 7.2 Hz, CH_3); MS (ESI) *m/z* 545 ($[M+H]^+$, 100%); Anal. Calcd for $C_{38}H_{32}N_4$: C, 84.00; H, 6.18; N, 10.25. Found: C, 83.79; H, 5.92; N, 10.29.

_N_,_N_'-Di(3-chloro-2-hydroxypropyl)-_N_,_N_'-di(9-ethyl-9_H_-carbazolyl)-2,7-diaminonaphthalene (4)

(A) A mixture of compound **3** (15 g, 28 mmol), epichlorohydrin (200 mL, 2.6 mol) and 75% acetic acid (20 mL) was stirred vigorously for 10 days at 30 °C. After termination of the reaction, the mixture was extracted with ethyl acetate, the organic layer washed with distilled water until neutral, then dried ($MgSO_4$), and the solvents were removed. The obtained compound **4** was used for the next step without purification.

(B) **5** (6 g, 9 mmol) was dissolved in dioxane (60 mL), and concentrated HCl (1.1 mL) was added dropwise at room temperature. The reaction mixture was stirred for 1.5 h, then treated with ethyl acetate (120 mL) and washed with distilled water until neutral. The organic layer was dried ($MgSO_4$), and the solvents were removed. The residue was purified by column chromatography (ethyl acetate/*n*-hexane = 3/1) to afford crystalline **4** (4.7 g, 70%), mp 201-203.5 °C; IR (KBr, cm^{-1}) 3384 (OH), 3049 (CH_{arom}), 2974, 2930, 2890 (CH_{aliph}), 1622, 1573 (C=C), 1230, 1154, 1139, 1122 (C-N), 821, 749 ($CH{=}CH_{arom}$); ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 8.02 (2H, br d, *J* = 7.5 Hz, 5-H of carbazole), 7.96 (2H, d, *J* = 1.8 Hz, 4-H of carbazole), 7.52-7.37 (8H, m, 1-H, 7-H and 8-H of carbazole, 4-H and 5-H of naphthalene), 7.33 (2H, dd, *J* = 8.7, 2.1 Hz, 2-H, of carbazole), 7.22, 7.20 (2H, two dd, *J* = 7.5, 1.2 Hz, 6-H of carbazole), 6.95 (2H, d, *J* = 2.1 Hz, 1-H and 8-H of naphthalene), 6.84 (2H, dd, *J* = 8.9, 2.1 Hz, 3-H and 6-H of naphthalene), 4.38 (4H, q, *J* = 7.2 Hz, $C\underline{H}_2CH_3$), 4.35-4.23 (2H, m, CH), 4.02 (4H, d, *J* = 6.6 Hz, $NC\underline{H}_2CH$), 3.78 (2H, dd, J_{AB} = 11.4 Hz, J_{AX} = 3.9 Hz, H_A of CH_2Cl), 3.69 (2H, dd, J_{AB} = 11.4 Hz, J_{BX} = 5.7 Hz, H_B of CH_2Cl), 2.58 (2H, br s, OH), 1.46 (6H, t, *J* = 7.2 Hz, CH_3); MS (ESI) *m/z* 729 ($[M+H]^+$, 70%); Anal. Calcd for $C_{44}H_{42}Cl_2N_4O_2$: C, 72.42; H, 5.80; N, 7.68. Found, %: C, 72.35; H, 5.78; N, 7.74.

_N_,_N_'-Di(9-ethyl-9H-carbazolyl)-_N_,_N_'-di(2-oxiranylmethyl)-2,7-diaminonaphthalene (5)

To a solution of **4** (13 g, 0.02 mol) in dioxane (50 mL), were added 85% powdered KOH (10 g, 1.2 mol) and anhydrous Na_2SO_4 (3 g, 20 mmol) in 5 equal portions every 30 min, and the mixture was stirred at room temperature for 3 hours. At the end of the reaction the mixture was treated with ethyl acetate and washed with distilled water until neutral. The organic layer was dried ($MgSO_4$), and the solvents were removed. The residue was dissolved in *THF* and kept at room temperature overnight. The formed crystals were filtered off, washed with diethyl ether and recrystallized from toluene to yield compound **5** (8.4 g, 70%), mp 201-203.5 °C; IR (KBr, cm^{-1}) 3048 (CH_{arom}), 2976, 2929, 2889 (CH_{aliph}), 1622, 1571 (C=C), 1229, 1154, 1139, 1121 (C-N),

820, 750 (CH=CH_{arom}); ^{1}H NMR (300 MHz, $CDCl_3$, *DMSO*-d_6, ppm) δ 8.05 (2H, d, J = 7.8 Hz, 5-H of carbazole), 8.00 (2H, d, J = 2.1 Hz, 4-H of carbazole), 7.56 (2H, d, J = 8.9 Hz, 4-H and 5-H of naphthalene 7.52 (2H, d, J = 8.7 Hz, 1-H of carbazole) 7.43 (2H, dd, J = 7.2, 1.2 Hz, 8-H of carbazole), 7.40, 7.38 (2H, two d, J = 7.2, 8.0 Hz, 7-H of carbazole), 7.32 (2H, dd, J = 8.7, 2.1 Hz, 2-H of carbazole), 7.15, 7.13 (2H, two dd, J = 8.0, 7.7, 1.2 Hz, 6-H of carbazole), 6.90 (2H, d, J = 2.4 Hz, 1-H and 8-H of naphthalene), 6.69 (2H, dd, J = 8.9, 2.4 Hz, 3-H and 6-H of naphthalene), 4.42 (q, 4H, J = 7.2 Hz, C$\underline{H_2}$CH$_3$), 4.08 (2H, dd, J_{AB} = 15.5 Hz, J_{AX} = 3.4 Hz, H_A of NC$\underline{H_2}$CH), 3.87 (2H, dd, J_{AB} = 15.5 Hz, J_{BX} = 5.2 Hz, H_B of NC$\underline{H_2}$CH), 3.30-3.25 (2H, m, CH), 2.73 (2H, dd, $J_{A'B'}$ = 5.1 Hz, $J_{A'X'}$ = 4.1 Hz, $H_{A'}$ of CH_2 from epoxy gr.), 2.57 (2H, dd, $J_{A'B'}$ = 5.1 Hz, $J_{B'X'}$ = 2.6 Hz, $H_{B'}$ of CH_2 from epoxy gr.), 1.37 (6H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, *DMSO*-d_6, ppm) δ 147.27, 139.80, 138.88, 137.01, 135.72, 127.56, 125.56, 125.23, 122.92, 121.84, 121.01, 120.21, 118.40, 114.78, 109.63, 108.72, 106.97, 54.36, 49.84, 44.91, 36.94, 13.57; MS (ESI) *m/z* 657 ([M+H]$^+$, 100%); Anal. Calcd for $C_{44}H_{40}N_4O_2$:C, 80.65; H, 6.28; N, 8.71. Found, %: C, 80.46; H, 6.14; N, 8.53.

1,8-Bis(9-ethyl-9*H*-carbazol-3-yl)-1,2,3,4,5,6,7,8-octahydroquino[5,6-*f*]quinoline-3,6-diol (6)

(A) A mixture of compound **3** (3.3 g, 6 mmol), epichlorohydrin (30 mL, 0.4 mol) and 75% acetic acid (2.5 mL) was refluxed under an argon atmosphere for 25 h. The crystalline product was filtered off, washed with diethyl ether and recrystallized from dioxane to yield **6** (2.5 g, 63%), mp 310-312°C. IR (KBr, cm^{-1}) 3273 (OH), 3048 (CH_{arom}), 2974, 2928, 2889, 2866, 2842 (CH_{aliph}), 1597 (C=C), 1220, 1154, 1139, 1122 (C-N), 819, 746 (CH=CH_{arom}); ^{1}H NMR (300 MHz, *DMSO*-d_6, CS_2, ppm) δ 8.06 (2H, d, J = 7.8 Hz, 5-H of carbazole), 7.99 (2H, d, J = 2.1 Hz, 4-H of carbazole) 7.97 (2H, d, J = 2.1 Hz, 4-H of carbazole of the other diastereomer), 7.58 (2H, d, J = 9.0 Hz, 1-H of carbazole), 7.55 (2H, d, J = 8.9 Hz, 8-H of carbazole), 7.45, 7.42 (2H, two d, J = 7.8, 8.9 Hz, 7-H of carbazole), 7.35 (1H, dd, J = 9.0, 2.1 Hz, 2-H of carbazole), 7.32 (1H, dd, J = 9.0, 2.1 Hz, 2-H of carbazole of the other diastereomer) 7.16, 7.14 (2H, two d, J = 7.8 Hz, 6-H of carbazole), 7.09 (1H, d, J = 8.9 Hz, 4-H and 5-H of naphthalene moiety), 7.08 (1H, d, J = 8.9 Hz, 4-H and 5-H of naphthalene moiety of the other diastereomer), 6.49 (2H, d, J = 8.9 Hz, 3-H and 6-H of naphthalene moiety), 5.17 (1H, d, J = 4.3 Hz, OH), 4.96 (1H, d, J = 4.3 Hz, OH of the other diastereomer), 4.45 (4H, q, J = 7.2 Hz, C$\underline{H_2}$CH$_3$), 4.24-4.14 (m, 1H, CH), 4.11-3.99 (m, 1H, CH of the other diastereomer), 3.84-3.24 (8H, m, CH_2 of tetrahydroquinoline), 1.39 (6H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, *DMSO*-d_6, ppm) δ 144.06, 141.08, 139.95, 136.88, 136.83, 125.78, 124.83, 124.69, 123.00, 122.96, 121.93, 120.54, 118.54, 117.85, 112.95, 112.40, 109.99, 109.09, 63.60, 63.16, 57.65, 36.98, 13.74; MS (ESI) *m/z* 657 ([M+H]$^+$, 100%); Anal. Calcd for $C_{44}H_{40}N_4O_2$: C, 80.37; H, 6.30; N, 8.67. Found, %: C, 80.46; H, 6.14; N, 8.53.

(B) A mixture of compound **4** (1.4 g, 2 mmol) and epichlorohydrin (35 mL) was refluxed under an argon atmosphere for 3 hours. The mixture was cooled and kept at room temperature overnight. The crystalls were filtered off, washed with 2-propanol and diethyl ether and recrystallized from dioxane to obtain **6** (0.7 g, 54%).

Acknowledgements

Financial support of this research by the Lithuanian Science and Studies Foundation is gratefully acknowledged.

References

1. Katritzky, A. R.; Rachwal, S.; Rachwal, B. *Tetrahydron* **1996**, *52*, 15031.
2. Perry, N. B.; Blunt, J. W.; Mc Combs, J. D.; Munro, M. H. G. *J. Org. Chem.* **1986**, *51*, 5476.
3. Perry, N. B.; Blunt, J. W.; Munro, M. H. G. *Tetrahedron* **1988**, *44*, 1727.
4. Nishiyama, S.; Cheng, J. F.; Tao, X. L.; Yamamura, S. *Tetrahedron Lett.* **1991**, *32*, 4151.
5. Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Yakura, T. *J. Am. Chem. Soc.* **1992**, *114*, 2175.
6. White, J. D.; Yager, K. M.; Yakura, T. *J. Am. Chem. Soc*. **1994**, *116*, 1831.
7. Kokwaro, G. O.; Taylor, G. *Drug Chem. Toxicol*. **1990**, *13*, 347.
8. Francis, C. L.; Ward, A. D. *Aust. J. Chem.* **1994**, *47*, 2109.
9. Omura, S.; Nakagawa, A. *Tetrahedron Lett*. **1981**, *22*, 2199.
10. Tsushima, K.; Osumi, T.; Matsuo, N.; Itaya, N. *Agric. Biol. Chem*. **1989**, *53*, 2529.
11. Nishiyama, T.; Hashiguchi, Y.; Sakata, T.; Sakaguchi, T. *Polymer Degradation and Stability* **2003**, *79*, 225.
12. Shikhaliev, K. S.; Shmyreva, Z.; Gurova, E. M. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Technol.* **1989**, *32*, 85; *Chem. Abstr*. **1990**, *112*, 216659a.
13. Rechardt, C.; Harms, K.; Kinzel, M.; Schafer, G.; Stein, J.; Wocadlo, S. *Liebigs. Ann.* **1995***,* 317.
14. Getautis, V.; Stanisauskaite, A.; Malinauskas, T.; Stumbraite, J.; Gaidelis, V.; Jankauskas, V. *Monatsh. Chem.* **2006**, *137***,** 1401.
15. Getautis, V; Stumbraite, J.; Gaidelis, V.; Jankauskas, V.; Kliucius, A.; Paulauskas, V. *Synth. Met.* **2007**, *157*, 35.
16. Meragelman, K. M.; West, L. M.; Northcote, P. T.; Pannell, L. K.; McKee, T. C.; Boyd, M. R. *J. Org. Chem.* **2002**, *67*, 6671.
17. Bergman, J.; Janosik, T.; Wahlström, N. *Adv. Heterocycl. Chem.* **2001**, *80*, 1.
18. Bjeldanes, L.; Kim, J.; Grose, K.; Bartholomew, J.; Bradfield, C. *Proc. Natl Acad. Sci. USA* **1991**, *88*, 9543.
19. Lygaitis, R.; Getautis, V.; Grazulevicius, V. J. *Chem. Soc. Rev.* **2008**, *37*, 770.
20. Olkhovik, V. K.; Vasilevskii, D. A.; Pap, A. A.; Kalechyts, G. V.; Matveienko, Y. V.; Baran, A. G.; Halinouski, N. A.; Petushok, V. G. *ARKIVOC* **2008**, (*ix*), 69.
21. Getautis, V.; Stanisauskaite, A.; Degutyte, R.; Stumbraite, J. *Monatsh. Chem.* **2007**, *138*, 1293.
22. Degutyte, R.; Stumbraite, J.; Getautis, V. *ARKIVOC* **2009**, *(vii)*, 26.