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LETTERS TO THE EDITOR

Synthesis and Amination of Oligo(trifluoromethanesulfonyl)dinaphthylmethanes

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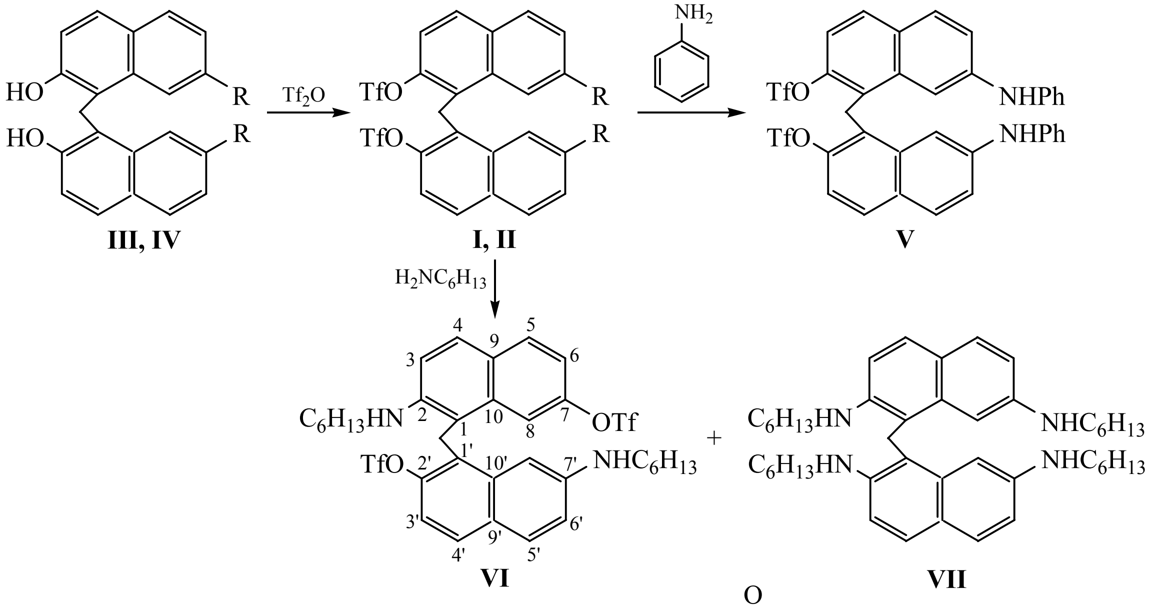
It was previously shown that the direct amination of 2,2',7,7'-tetrahydroxydinaphthylmethane with primary amines proceeds via the C–C bonds cleavage and the elimination of the methylene unit [1]. At the same time it is known that the catalytic amination of triflate derivatives of phenols and naphthols occurs under mild conditions to give aromatic amines [2–4]. In the present work we reported the first data on the synthesis of 2,2',7,7'-tetratriflato- (**I**) and 2,2'-di(trifluoromethanesulfonyl)dinaphthylmethanes (**II**) and their subsequent amination.

Oligotrifluoromethanesulfonyldinaphthylmethanes **I** and **II** were prepared by the reaction of oligohydroxydinaphthylmethanes **III** and **IV** with trifluoromethanesulfonic anhydride in pyridine at 0°C with the yield of 67 and 78%, respectively.

The ^{19}F NMR spectrum of 2,2'-ditriflate **II** contains a singlet at δ –73.2 ppm. In the ^{19}F NMR spectrum of 2,2',7,7'-tetratriflate **I** there are two singlet signals at δ –72.9 and –73.2 ppm owing to the nonequivalent triflate groups located at positions 2 and 7. In the ^{1}H NMR spectrum of compounds **I** and **II** there are no signals of hydroxy protons, and the well-resolved signals of the protons of dinaphthylmethane frame are observed. The ^{13}C NMR spectrum of compound **I** contains two downfield singlets at δ 146.39 and



R = OTf (**I**), H (**II, IV**), OH (**III**); Tf = $-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-CF_3$.

148.34 ppm originating from the carbon atoms bonded to the triflate groups. In the spectrum of **II** there is a singlet at δ 145.6 ppm. The data of elemental analysis confirm the presence of triflate fragments in molecules **I** and **II**.

The amination of oligotrifluoromethanesulfonyldinaphthylmethanes **I** and **II** with aniline and hexylamine was carried out in pyridine in the presence of $Pd(OAc)_2$ and BINAP. The reaction of tetratriflate **I** with aniline affords 2,2'-ditrifluoromethanesulfonyl-7,7'-bis(phenylamino)dinaphthylmethane **V** in 70% yield. The presence of signals of the H and C atoms of methylene unit in the ^{1}H and ^{13}C NMR spectra of compound **V** indicate that the structure of the initial dinaphthylmethane is retained. The ratio of integral intensities of the aromatic protons signals in the ^{1}H NMR spectrum and MALDI data showed the substitution of two triflate groups with phenylamine fragments. The presence in the ^{19}F NMR spectrum of dinaphthylmethane **V** of a singlet signal at –73.2 ppm, similar to 2,2'-ditriflate **II,** and of the signals of carbon atoms connected with the amino (δ 143.1 ppm) and triflate (δ 146.3 ppm) groups in the ^{13}C NMR spectrum suggests that the substitution occurs at the carbon atoms $C^{7,7'}$. Further confirmation of this regionselectivity of the process is the absence of amination products in the reaction of 2,2'-ditrifluoromethanesulfonyldinaphthylmethane **II** with aniline.

The amination of tetratrifluoromethanesulfonyldinaphthylmethane **I** with hexylamine results in the formation of two products **VI** and **VII** containing two and four amino groups, respectively. The presence of two signals of triflate groups at δ_F –72.8 and –73.0 ppm in the ^{19}F NMR spectrum of 2,7'-bis(hexylamino)-2',7-ditrifluoromethanesulfonyldinaphthylmethane **VI** and a doubling of all signals of the naphthalene protons in ^{1}H NMR spectrum pointed to the asymmetry of the resulting molecule. In the ^{1}H NMR spectrum of the symmetric 2,2',7,7'-tetra(hexylamino)dinaphthylmethane **VII**) there is only one set of signals of aromatic protons. The elemental analysis data for compounds **VI** and **VII** agree with the above formulas.

Triflation of oligohydroxydinaphthylmethanes III and IV. To a solution of the corresponding oligohydroxydinaphthylmethane (0.3 mmol) in pyridine (3 ml) at 0ºC was added dropwise trifluoromethanesulfonic anhydride (2.8 mmol). The reaction mixture was kept at room temperature for 24 h, then to it 20 ml of water was added. The precipitate was filtered off, washed with 5% hydrochloric acid solution, then with water until a neutral reaction, and dried at 80–90°C (1 mm Hg).

2,2',7,7'-Tetra(trifluoromethanesulfonyl)dinaphthylmethane (I). Yield 67%, pale yellow powder, mp 113–114°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.01 s (2H, CH_2), 7.35 d.d (2H, H^6, $^3J_{HH}$ 9.2, $^4J_{HH}$ 2.3 Hz), 7.58 d (2H, H^3, $^3J_{HH}$ 9.2 Hz), 7.73 d (2H, H^8, $^4J_{HH}$ 1.8 Hz), 7.93 d (4H, $H^{4,5}$, $^3J_{HH}$ 9.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.48 (CH_2), 116.32 (C^8), 118.69 d (CF_3, $^1J_{CF}$ 320.5 Hz), 120.98 (C^3), 121.34 (C^6), 127.42 (C^1), 130.52 (C^4), 131.93 (C^5), 132.04 (C^{10}), 132.86 (C^9), 146.39 (C^2), 148.34 (C^7). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –72.86, –73.14. Found, %: C 34.77; H 1.08. $C_{25}H_{12}F_{12}O_{12}S_4$. Calculated, %: C 34.89; H 1.41.

2,2'-Di(trifluoromethanesulfonyl)dinaphthylmethane (II). Yield 78%, brown powder, 114–115°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.04 s (2H, CH_2), 7.37 d.d (2H, H^6, $^3J_{HH}$ 8.2, $^3J_{HH}$ 7.3 Hz), 7.45 d.d (2H, H^7, $^3J_{HH}$ 8.7, $^3J_{HH}$ 6.0 Hz), 7.47 d (2H, H^3, $^3J_{HH}$ 9.2), 7.83 d (4H, $H^{4,5}$, $^3J_{HH}$ 9.1 Hz), 7.84 d (4H, H^8, $^3J_{HH}$ 9.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C ppm: 24.66 (CH_2), 118.71 d (CF_3, $^1J_{CF}$ 319.2), 119.54 (C^3), 124.36 ($C^{4/5}$), 126.86 (C^7), 127.63 (C^1), 127.71 (C^6), 129.06 (C^8), 130.04 ($C^{4/5}$), 132.60 (C^{10}), 132.87 (C^9), 145.63 (C^2). ^{19}F NMR spectrum ($CDCl_3$): δ_F –73.17. Found, %: C 48.62; H 2.46. $C_{23}H_{14}F_6O_6S_2$. Calculated, %: C 48.94; H 2.50.

Amination of tetra(trifluoromethanesulfonyl)dinaphthylmethane I. A mixture of BINAP (0.019 mmol) and $Pd(OAc)_2$ (0.013 mmol) in toluene (10 ml) was heated for 5 min at 85°C while stirring under argon, then tetratriflate **I** (0.16 mmol), corresponding amine (1.95 mmol) and Cs_2CO_3 (1.95 mmol) were added. The mixture was heated at 110°C for 5 h. The precipitate was filtered off, the filtrate was concentrated, and the products were chromatographed (silica gel, benzene–hexane, 1:1) and dried at 90–100°C (1 mm Hg).

2,2'-Di(trifluorosulfonyl)-7,7'-(diphenylamino)dinaphthylmethane (V). Yield 70%, dark green powder, mp 164–165°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.76 s (2H, CH_2), 5.73 br.s (2H, NH), 6.90 d (4H, $H^{o\text{-Ph}}$, $^3J_{HH}$ 7.8 Hz), 7.03 t (2H, $H^{p\text{-Ph}}$, $^3J_{HH}$ 7.4 Hz), 7.06 d (2H, H^3, $^3J_{HH}$ 8.7 Hz), 7.08 d.d (2H, H^6, $^3J_{HH}$ 8.7, $^4J_{HH}$ 1.8 Hz), 7.15 d (2H, H^8, $^4J_{HH}$ 1.9 Hz), 7.25 d.d (4H, $H^{m\text{-Ph}}$, $^3J_{HH}$ 8.3, $^3J_{HH}$ 7.8 Hz), 7.62 d (2H, H^5, $^3J_{HH}$ 8.8 Hz), 7.64 d (2H, H^4, $^3J_{HH}$ 8.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C ppm: 24.76 (CH_2), 106.44 (C^8), 116.43 (C^3), 118.51 d (CF_3, $^1J_{CF}$ 322.5 Hz), 119.82 ($C^{o\text{-Ph}}$,C^6), 122.71 ($C^{p\text{-Ph}}$), 125.40 (C^9), 127.83 (C^1), 129.18 (C^4), 129.64 ($C^{m\text{-Ph}}$), 130.22 (C^4), 134.24 (C^{10}), 141.27 ($C^{i\text{-Ph}}$), 143.12 (C^7), 146.29 (C^2). ^{19}F NMR spectrum ($CDCl_3$): δ_F –73.19 ppm. Mass spectrum: *m*/*z* 808 [M^+ + K^+ + Na^+]. Found, %: C 59.31; N 3.23; H 3.69. $C_{41}H_{30}F_6N_2O_6S_2\cdot C_6H_6$. Calculated, %: C 59.70; N 3.40; H 3.67.

2,7'-Di(hexylamino)-2',7-di(trifluorosulfonyl)dinaphthylmethane (VI). Yield 12%, brown oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (6H, CH_3, $^3J_{HH}$ 6.7 Hz), 1.25–1.62 m [16H, $CH_2(C\mathit{H}_2)_4CH_3$), 2.89 t [4H, $C\mathit{H}_2(CH_2)_4CH_3$, $^3J_{HH}$ 7.1 Hz), 3.86 br.s (2H, NH), 4.91 s (2H, CH_2), 6.58 d (1H, $H^{8'}$, $^4J_{HH}$ 1.8 Hz), 6.76 d.d (1H, $H^{6'}$, $^3J_{HH}$ 8.7, $^4J_{HH}$ 1.8 Hz), 7.15 d (1H, H^3, $^3J_{HH}$ 9.2 Hz), 7.33 d.d (1H, H^6, $^3J_{HH}$ 9.2, $^4J_{HH}$ 2.2 Hz), 7.54 d (2H, $H^{5',3'}$, $^3J_{HH}$ 8.7 Hz), 7.64 d (1H, H^4, $^3J_{HH}$ 8.7 Hz), 7.80 d (1H, H^8, $^4J_{HH}$ 2.3 Hz), 7.87 d (1H, $H^{4'}$, $^3J_{HH}$ 7.4 Hz), 7.89 d (1H, H^5, $^3J_{HH}$ 7.4 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –72.79, –73.04, –73.29. Mass spectrum: *m*/*z* 1044 [M^+ + $C_2F_6O_5S_2$].

2,2',7,7'-Tetra(hexylamino)dinaphthylmethane (VII). Yield 4%, brown oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (12H, CH_3, $^3J_{HH}$ 6.9 Hz), 1.23–1.62 m [32H, $CH_2(C\mathit{H}_2)_4CH_3$], 2.84 t [8H, $C\mathit{H}_2(CH_2)_4\cdot CH_3$, $^3J_{HH}$ 6.9 Hz), 3.69 br.s (4H, NH), 4.82 s (2H, CH_2), 6.69 d (2H, H^8, $^4J_{HH}$ 1.9 Hz), 6.73 d.d (2H, H^6, $^3J_{HH}$ 8.7, $^4J_{HH}$ 2.2 Hz), 7.12 d (2H, H^3, $^3J_{HH}$ 9.2 Hz), 7.51 d (2H, H^5, $^3J_{HH}$ 8.7 Hz), 7.59 d (2H, H^4, $^3J_{HH}$ 9.2 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –73.26 ppm. Mass spectrum: *m*/*z* 946 [M^+ + $C_2F_6O_5S_2$].

^{1}H and ^{13}C NMR spectra were registered on a Jeol ECX-400 spectrometer operating at 400 (^{1}H) and 100.5 MHz (^{13}C) with internal reference TMS. The mass spectra were recorded on a KRATOS KOMPACT instrument (MALDI–TOF MS), matrix 1,8,9-trihydroxyanthracene. The elemental analysis was performed on a CHN-analyzer Eager 300.

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