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Arkivoc **2019**, part v, 89-95

Transformations of perfluorotoluene by the action of 2-mercaptoethanol

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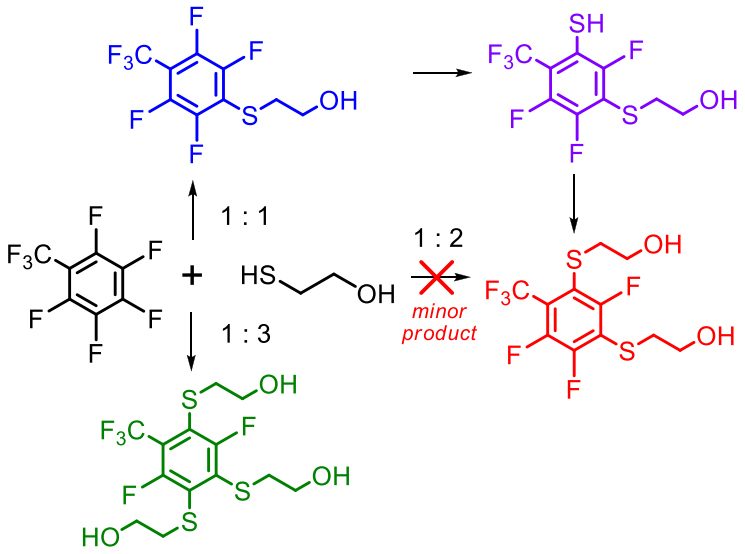
Dedicated to the memory of academician D.G. Knorre

Received 09-10-2018 **Accepted** 12-14-2018 **Published on line** 02-19-2019

Abstract

The reaction of perfluorotoluene and 2-mercaptoethanol in the presence of K_2CO_3 in DMF has been studied and experimental procedures for selective introduction of one, two and three ethanolthiyl groups into perfluorotoluene have been elaborated.



Keywords: Perfluorotoluene, 2-mercaptoethanol, aromatic nucleophilic substitution, regioselectivity

DOI: https://doi.org/10.24820/ark.5550190.p010.747

Introduction

For the last few decades, intensive investigations have been devoted to materials that demonstrate non-linear optical (NLO) properties and various strategies for the synthesis of dendrimer materials with NLO properties have been described.[1-3] Moreover, some results provide evidence that the correct choice of 'a suitable isolation group' might have a strong influence on the macroscopic NLO properties in polymers.[4] For example, the introduction of polyfluoroarenes as isolation groups improves the stability and enhances the second harmonic coefficient d_{33}.[5,6] It was also shown that tetrafluorophenylene-linkages compared to non-fluorinated ones provided higher quantum yields of fluorescence, but with smaller two-photon absorptivity.[7] The use of fluorinated species can also aid in the formation of non-covalent interactions that improve the organization of the molecules in the crystal phase and thus the electrooptic properties.[4,8] For these reasons, a notable number of studies were devoted to the synthesis of polyfluorinated arylenes.[9-12] Recently, a versatile method for construction of fluorinated poly(aryl thioethers) was developed based on organo-catalyzed nucleophilic aromatic substitution of silyl-protected dithiols.[13]

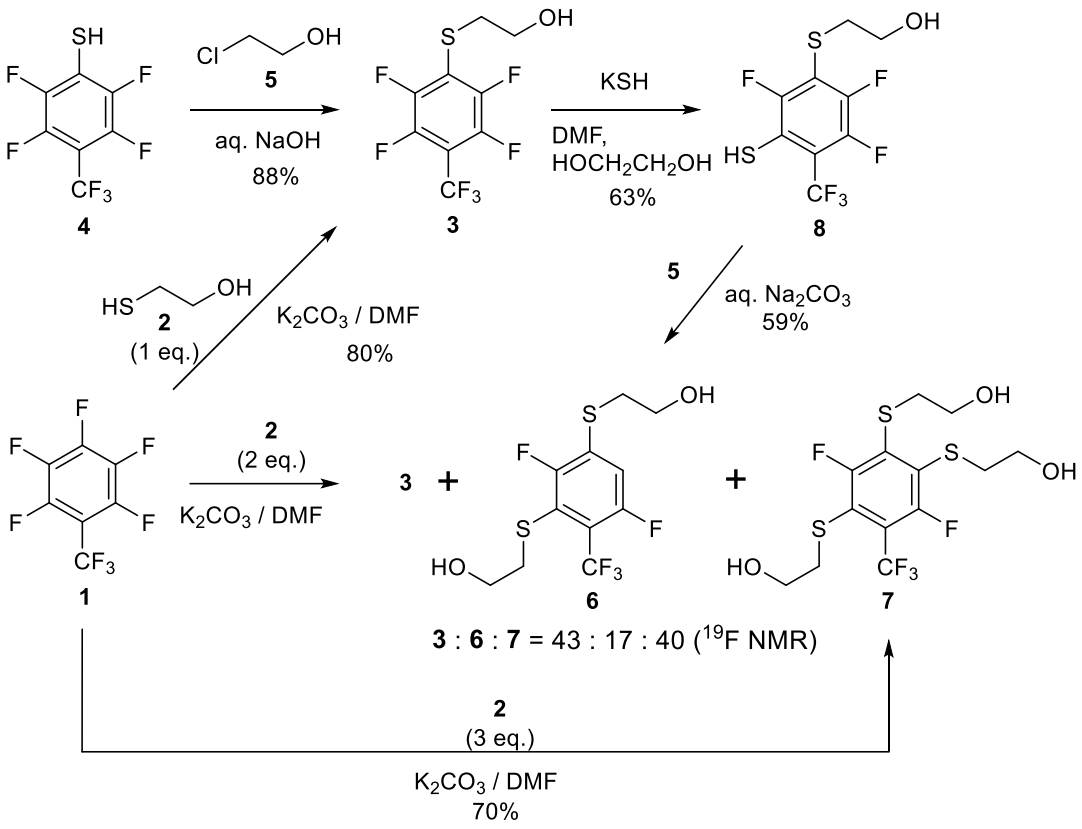
The current work investigates the transformations of perfluorotoluene under the action of 2-mercaptoethanol and has been aimed at the synthesis of substituted derivatives of perfluorotoluene as potential blocks for dendrimer construction. The study focused on the regioselectivity of the reaction and elaboration of reliable synthetic procedures. 2-Mercaptoethanol was selected because its hydroxyl groups enable the further functionalization of the products while the sulfur can be oxidized to either the sulfoxide or sulfone state. Examples of the reactions of polyfluoroarenes with excess of S-nucleophiles are known.[14-16]

Results and Discussion

The reaction of perfluorotoluene (**1**) with an equimolar amount of 2-mercaptoethanol (**2**) in the presence of potassium carbonate afforded 2-{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]thio}ethan-1-ol (**3**). Potassium carbonate was used to transform thiol **2** to an even more nucleophilic thiolate-anion. The direction of aromatic nucleophilic fluorine substitution was typical for the reactions of subsituted pentafluorophenyls (C_6F_5X) with various nucleophiles.[17] Recently, kinetics for the nucleophilic aromatic monosubstitution of *para*-fluorine by the action of thiol **2** in aq. MeCN were measured for a series of polyfluoroarenes C_6F_5X, including compound **1**.[18] Compound **3** was also obtained by alkylation of 2,3,5,6-tetrafluoro-4-trifluoromethyl-benzenethiol (**4**) by 2-chloroethanol (**5**) in aqueous alkali.

When arene **1** reacted with thiol **2** (2 equiv), a mixture of mono- (**3**), di- (**6**) and trisubstituted (**7**) perfluorotoluenes in the ratio 43 : 17 : 40 (^{19}F NMR) was formed, while the action of 3 equivalents of thiol **2** to compound **1** afforded exclusively trisubstituted compound **7** (70%) in a one-pot procedure. On the one hand, the nucleophilic substitution of fluorine at the C3 position of compound **3** was well known and the regioselectivity was attributed to the directing effects of the electron-withdrawing trifluoromethyl and electron-donating alkanethiyl groups. On the other hand, the introduction of one more alkanethiyl group assists the subsequent nucleophilic substitution of fluorine in the *para*-position to it (**6**, ^{6}F) with formation of compound **7**.[16] The analogous reaction pathway has been observed in reactions of other polyfluoroarenes. For example, the reaction of 1,2,4,5-tetrafluorobenzene with sodium *tert*-butylthiolate gave 1,4-bis(*tert*-butylthio)-2,5-difluorobenzene in 87% yield.[19] Transformations of hexafluorobenzene under the action of sodium isopropylthiolate or cesium propylthiolate led to the formation of 1,4-bis(isopropylthio)-2,3,5,6-tetrafluorobenzene and 1,4-bis(propylthio)-2,3,5,6-tetrafluorobenzene in 71 and 81% yields, respectively.[19,20]

Furthermore, the reaction of a 1:1 ratio of hexafluorobenzene with 2-mercaptoethanol (**2**) or sodium 2-hydroxyethanethiolate in liquid ammonia gave exclusively the 2,2'-(perfluoro-1,4-phenylene)bis(sulfanediyl)-diethanol in ~100% yield[21] which was consistent with our results. The observed results were attributed to the greater polarizability of the sulfur than fluorine atom.[22] A structure specific synthesis of the disubstituted product **6** was achieved from compound **3** in 2 steps: arene **3** was reacted with potassium hydrosulfide to afford thiol **8**, which was subsequently treated with 2-chloroethanol (**5**) (Scheme 1).



Scheme 1. Synthesis of mono- (**3**), di- (**6**) and trisubstituted (**7**) polylfluoroarenes from perfluorotoluene (**1**) and 2-mercaptoethanol (**2**)

Conclusions

The selective introduction of one, two and three 2-hydroxyethylthio groups into perfluorotoluene has been realized and the regioselectivity of the process has been revealed. The results add to the experimental data on the aromatic nucleophilic substitution in polyfluoroarenes by the action of S-centered nucleophiles. The approach will be useful for the synthesis of branched structures with 1,2,4-trisulfanyl substitution patterns in polyfluorinated benzene cores.

Experimental Section

General. Analytical measurements. The NMR spectra of reaction mixtures or individual compounds were recorded on Bruker AVANCE 300 [300.13 (^{1}H), 282.4 (^{19}F) MHz], Bruker AV-400 [400.13 (^{1}H), 100.6 (^{13}C) MHz] or Bruker DRX-500 [500.13 (^{1}H), 125.76 (^{13}C) MHz] spectrometers for solutions of samples in CCl_4, $(CD_3)_2CO$, or CD_3CN [for ^{1}H and ^{19}F], $CDCl_3$ [for ^{1}H, ^{13}C and ^{19}F] or CD_3CN [for ^{13}C and ^{19}F]. NMR coupling constants (*J*) were measured in Hertz (Hz). IR spectra were recorded on a spectrophotometer Bruker Vector 22 from pellets with KBr for solid and from films for liquid samples. UV spectra were obtained on a spectrophotometer Hewlett Packard 8453 from solutions in ethanol. The molecular mass and elemental composition was determined from the high resolution mass spectra taken on Thermo Electron Corporation DFS instrument (ionizing electrons energy 70 eV). Elemental analysis was performed on an EURO EA 3000 automatic CHNS analyzer.[23] Fluorine determination was performed spectrophotometrically using a Cary-50 spectrophotometer. GC-MS spectra were measured on Hewlett-Packard G1081A instrument equipped with a gas chromatograph HP 5890 Series II and a mass-selective detector HP 5971 (EI, 70 eV), capillary column HP-5 (5% of diphenyl-, 95% dimethylsiloxane) 30 m × 0.25 mm × 0.25 μm, carrier gas helium, flow rate 1 mL/min. Injector temperature 280 °C, ion source temperature 173 °C. Scanning rate 1.2 scan/s in mass region 30–650 a.u.m. Analytic GLC was carried out on a chromatograph Hewlett Packard 5980, equipped with a quartz capillary column HP-5 (stationary phase dimethyl diphenyl polysiloxane block copolymer), 30 m × 0.52 mm × 2.6 μm, and a thermal conductivity detector (TCD). The melting points were measured on a Koeffler heating block and are uncorrected.

All starting compounds are widely used commercially available products of reagent grade and purified in the usual manner whenever necessary prior to use. Perfluorotoluene (**1**, 97%) was obtained from P&M Invest, and 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzenethiol (**4**) was obtained from compound **1** according to described procedure.[24]

2-{[2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl]thio}ethan-1-ol (3). Procedure A. Reaction of perfluorotoluene (**1**) and 2-mercaptoethanol (**2**) in ratio 1:1. Compound **2** (11.44 g, 145.96 mmol) was added to the solution of arene **1** (33.82 g, 141.84 mmol) in DMF (290 mL) in the presence of K_2CO_3 (21.24 g, 152.14 mmol). After 4.5 h stirring at room temperature the resulted mixture was poured into 5% aq. HCl (500 mL), the organic layer was washed with water (2 × 250 mL) and dried ($MgSO_4$). The crude product (35.28 g, 95% GLC, 80% yield) was purified by vacuum distillation.

Procedure B. Alkylation of 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzenethiol (**4**) by 2-chloroethanol (**5**). Arenethiol **4** (4.54 g, 18.2 mmol) was dissolved in 1 M NaOH (20 mL), then compound **5** (3.54 g, 44.0 mmol) was added. After stirring overnight at room temperature, the mixture was extracted with $CHCl_3$ (2 × 10 mL), washed with water (2 × 50 mL), dried ($MgSO_4$) and the solvent was evaporated to give compound **3** (4.69 g, 88%) as a colorless oil, mp 16-17 °C. bp 83-85 °C (2 Torr). IR (neat, ν_{max}, cm^{-1}) 3360(w), 2945(w), 2884(w), 1647(m), 1479(s), 1398(w), 1329(s), 1182(m), 1148(s), 1063(w), 980(s), 831(m), 716(m). UV, λ_{max}, nm (log ε): 209 (3.87), 279 (3.81). ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ_H 2.66 (br.s, 1H, OH), 3.18 (t, $^3J_{HH}$ 5.9, 2H, CH_2S), 3.75 (t, $^3J_{HH}$ 5.9, 2H, CH_2O). ^{13}C NMR ($CDCl_3$, 125.76 MHz), δ_C 37.2 (t, $^4J_{CF}$ 3.2, S$\underline{C}H_2$), 61.4 (O$\underline{C}H_2$), 109.2 (qt, $^2J_{CF}$ 35.1, $^2J_{CF}$ 12.9, $\underline{C}_{Ar}CF_3$), 119.8 (t, $^2J_{CF}$ 19.9, $\underline{C}_{Ar}S$), 121.0 (q, $^1J_{CF}$ 228.9, $\underline{C}F_3$), 143.0-145.4 (m, $\underline{C}_{Ar}F$), 146.0-148.2 (m, $\underline{C}_{Ar}F$). ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -141.5 - -141.1 [m, 2F, F-(2,6)], -133.5 - -133.3 [m, 2F, F-(3,5)], -57.7 (t, $^4J_{FF}$ 21.7, 3F, CF_3). Anal. calcd for $C_9H_5F_7OS$, %: C 36.75; H 1.71; F 45.21; S 10.90; *m/z* 293.9944. Found, %: C 36.76; H 1.83; F 45.24; S 10.85; *m/z* 293.9937.

2,2'-{[2,4,5-Trifluoro-6-(trifluoromethyl)-1,3-phenylene]bis(sulfanediyl)}diethanol (6). Reaction of perfluorotoluene (1) and 2-mercaptoethanol (2) in ratio 1:2. Compound **2** (0.88 g, 11.3 mmol) was added to the solution of arene **1** (1.32 g, 5.59 mmol) in DMF (5 mL) in the presence of K_2CO_3 (1.54 g, 11.2 mmol). After 24 h stirring at 20-25 °C the resulted mixture was acidified with aq. HCl and subjected to analysis by means of ^{19}F NMR, which revealed compounds **3**, **6** and **7** in ratio 43 : 17 : 40 (^{19}F NMR).

2-{[2,3,6-Trifluoro-5-mercapto-4-(trifluoromethyl)phenyl]thio}ethanol (8). A solution of potassium hydrosulfide in 1,2-ethanediol (4 M, 41 mL, *ca.* 164 mmol) was prepared according to a previously described procedure[24] and was added dropwise to a solution of compound **3** (25.7 g, 98%, 85.61 mmol) in DMF (155 mL) for 35 min at 24-28 °C and the reaction mixture was stirred for 2 h at 28-23 °C, poured into 15% aq. HCl (300 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The extract was washed with water (3 × 50 mL) and dried ($MgSO_4$). The solvent was distilled off, and the residue was crystallized to give thiol **8** (16.64 g, 63%) as a colorless solid, mp 32-33 °C. IR (KBr, ν_{max}, cm^{-1}): 3288(m), 2956(w), 2939(w), 2877(w), 2611(w), 1616(w), 1568(w), 1454(s), 1412(m), 1356(s), 1279(s), 1194(m), 1173(s), 1142(s), 1128(s), 1068(s), 1014(m), 964(w), 947(m), 866(s), 773(m), 742(w), 723(m), 696(m), 665(w), 644(w). UV, λ_{max}, nm (log ε): 210 (4.25), 240 (3.97), 274 (3.98), 353 (3.18). ^1H NMR ($CDCl_3$, 500.13 MHz): δ_H 1.78 (br.s, 1H, OH), 3.14 (t, $^3J_{HH}$ 6.0, 2H, CH_2S), 3.71 (t, $^3J_{HH}$ 6.0, 2H, CH_2O), 4.08 (qd, $^5J_{HF}$ 8.0, $^4J_{HF}$ 8.0, 1H, SH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 37.3 (t, $^3J_{CF}$ 2.8, $\underline{C}H_2S$), 61.2 ($\underline{C}H_2O$), 116.6 (qdd, $^2J_{CF}$ 33.2, $^2J_{CF}$ 10.6, $^3J_{CF}$ 2.0, $\underline{C}CF_3$), 117.2 [dd, $^2J_{CF}$ 26.4, $^3J_{CF}$ 4.4, $\underline{C}$-(5)S], 117.8 [dd, $^2J_{CF}$ 27.5, $^2J_{CF}$ 19.0, $\underline{C}$-(1)S], 122.2 (qd, $^1J_{CF}$ 276.0, $^3J_{CF}$ 1.3, $\underline{C}F_3$), 146.2 [ddq, $^1J_{CF}$ 261.2, $^2J_{CF}$ 16.9, $^3J_{CF}$ 1.8, $\underline{C}$-(3)F], 148.5 [ddd, $^1J_{CF}$ 247.8, $^2J_{CF}$ 14.9, $^3J_{CF}$ 5.7, $\underline{C}$-(2)F], 152.9 [ddd, $^1J_{CF}$ 237.9, $^3J_{CF}$ 3.5, $^4J_{CF}$ 3.5, $\underline{C}$-(6)F]. ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ_F -139.9 [qdd, $^4J_{FF}$ 26.4, $^4J_{FF}$ 21.9, $^5J_{FF}$ 13.6, F-(3)], -131.6 [dd, $^3J_{FF}$ 21.9, $^4J_{FF}$ 2.0, F-(2)], -102.6 [dddq, $^5J_{FF}$ 13.6, $^4J_{FH}$ 8.0, $^4J_{FF}$ 2.0, $^5J_{FF}$ 2.0, F-(6)], -57.6 (ddd, $^4J_{FF}$ 26.4, $^5J_{FH}$ 8.5, $^5J_{FF}$ 2.0, 3F, CF_3). Anal. calcd. for $C_9H_6F_6OS_2$: C 35.07; H 1.96; F 36.98; S 20.80; *m/z* 307.9759. Found: C 35.38; H 2.08; F 37.01; S 21.03; *m/z* 307.9755.

2,2'-{[2,4,5-Trifluoro-6-(trifluoromethyl)-1,3-phenylene]bis(sulfanediyl)}diethanol (6). Alkylation of thiol 8 by 2-chloroethanol (5). Compound **5** (2.05 g, 25.5 mmol) was dissolved in H_2O (35 mL) and added dropwise to a solution of thiol **8** (7.71 g, 25.0 mmol) and Na_2CO_3 (1.98 g, 18.5 mmol) in H_2O (35 mL) for a period of 15 min at 44-39 °C. The resulting solution was stirred at 39-50 °C for 9 h, then cooled, extracted with CH_2Cl_2 (2 × 10 mL) and dried ($MgSO_4$). The solvent was distilled off and the residue was crystallized to give product **6** (5.94 g, 59% yield) as colorless solid, mp (CH_2Cl_2) 56–57 °C. IR (KBr, ν_{max}, cm^{-1}): 3373(m), 2943(w), 2912(w), 2887(w), 1603(w), 1450(s), 1412(m), 1350(s), 1302(w), 1271(m), 1248(w), 1182(s), 1146(s), 1082(m), 1063(s), 1020(m), 1005(w), 955(m), 876(m), 729(w), 702(m), 683(w), 661(w), 650(w). UV, λ_{max}, nm (log ε): 219 (4.08), 284 (3.82). ^1H NMR [$(CD_3)_2CO$, 300.13 MHz], δ_H 3.06 (t, $^3J_{HH}$ 6.5, 2H, CH_2S), 3.22 (t, $^3J_{HH}$ 6.2, 2H, CH_2S), 3.63-3.83 (m, 4H, $2CH_2O$), 3.93 (t, $^3J_{HH}$ 5.6, 1H, OH), 4.05 (t, $^3J_{HH}$ 5.6, 1H, OH). ^{13}C NMR (CD_3CN, 100.6 MHz): δ_C 37.4 [t, $^4J_{CF}$ 3.0, CH_2S-(3)], 39.0 [d, $^4J_{CF}$ 4.6, $\underline{C}H_2S$-(1)], 61.8 ($\underline{C}H_2O$), 62.0 ($\underline{C}H_2O$), 119.1 [dd, $^2J_{CF}$ 25.1, $^3J_{CF}$ 4.0, $\underline{C}$-(1)], 120.1 [dd, $^2J_{CF}$ 27.7, $^2J_{CF}$ 18.7, $\underline{C}$-(3)], 121.2 [qd, $^2J_{CF}$ 30.6, $^2J_{CF}$ 5.9, $\underline{C}$-(6)], 123.2 (qd, $^1J_{CF}$ 274.8, $^3J_{CF}$ 2.7, $\underline{C}F_3$), 146.5 [ddd, $^1J_{CF}$ 259.9, $^2J_{CF}$ 16.9, $^4J_{CF}$ 2.7, $\underline{C}$-(5)], 152.3 [ddd, $^1J_{CF}$ 248.0, $^2J_{CF}$ 15.4, $^3J_{CF}$ 6.0, $\underline{C}$-(4)], 160.2 [dt, $^1J_{CF}$ 239.9, $^3J_{CF}$ 3.3, $\underline{C}$-(2)]. ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ_F -149.0 [qdd, $^4J_{FF}$ 34.6, $^3J_{FF}$ 21.9, $^5J_{FF}$ 13.6, F-(5)], -124.5 [dd, $^3J_{FF}$ 21.9, $^4J_{FF}$ 5.1, F-(4)], -97.5 [dd, $^5J_{FF}$ 13.6, $^4J_{FF}$ 5.1, F-(2)], -55.7 (d, $^4J_{FF}$ 34.6, 3F, CF_3). Anal. cacld. for $C_{11}H_{10}F_6O_2S_2$: C 37.50; H 2.86; F 32.36; S 18.20; *m/z* 352.0021. Found: C 37.24; H 2.70; F 32.31; S 18.22; *m/z* 352.0018.

2,2',2''-{[3,6-Difluoro-5-(trifluoromethyl)benzene-1,2,4-triyl]tris(sulfanediyl)}triethanol (7). **Reaction of perfluorotoluene (1) and 2-mercaptoethanol (2) in ratio 1:3**. Compound **2** (1.19 g, 15.1 mmol) was added to the solution of arene **1** (1.17 g, 4.91 mmol) in DMF (12 mL) in the presence of K_2CO_3 (1.61 g, 11.5 mmol). After 8.5 h stirring at 20-25 °C the resulting mixture was poured into 5% aq. HCl (50 mL). The precipitate was filtered off, dried over P_2O_5 and recrystallized to give compound **7** (1.42 g, 70% yield). Colorless powder, mp 58–60 °C (CH_2Cl_2). IR (KBr, ν_{max}, cm^{-1}): 3522(s), 3361(s), 2941(m), 2922(m), 2883(m), 2870(m), 1610(w), 1568(m),

1525(m), 1454(m), 1431(m), 1400(s), 1385(s), 1294(s), 1257(s), 1203(m), 1184(s), 1140(s), 1128(s), 1055(s), 1014(s), 945(w), 926(w), 860(s), 690(w), 660(m), 631(m). UV, λ_{max}, nm (log ε): 234 (4.15), 273 (3.97), 325 (3.91). ^{1}H NMR [$(CD_3)_2CO$, 400.13 MHz]: δ_H 3.11 (t, $^{3}J_{HH}$ 6.4, 2H, CH_2S), 3.14 (t, $^{3}J_{HH}$ 6.3, 2H, CH_2S), 3.26 (t, $^{3}J_{HH}$ 6.1, 2H, CH_2S), 3.66-3.76 (m, 6H, $3CH_2O$), 3.99 (t, $^{3}J_{HH}$ 5.4, 1H, OH), 4.04 (t, $^{3}J_{HH}$ 5.7, 1H, OH), 4.11 (t, $^{3}J_{HH}$ 5.6, 1H, OH). ^{13}C NMR (CD_3CN, 100.6 MHz): δ_C 38.3 (d, $^{4}J_{CF}$ 8.1, $\underline{C}H_2S$), 38.7 (d, $^{4}J_{CF}$ 5.3, $\underline{C}H_2S$), 38.8 (d, $^{4}J_{CF}$ 5.9, $\underline{C}H_2S$), 61.7 ($\underline{C}H_2O$), 61.8 ($\underline{C}H_2O$), 61.9 ($\underline{C}H_2O$), 119.9 [qd, $^{2}J_{CF}$ 30.8, $^{2}J_{CF}$ 13.6, $\underline{C}$-(5)], 123.5 (qdd, $^{1}J_{CF}$ 275.1, $^{3}J_{CF}$ 2.7, $^{4}J_{CF}$ 2.7, $\underline{C}F_3$), 124.6 (d, $^{2}J_{CF}$ 26.6, $\underline{C}_{Ar}S$), 129.9 (dd, $^{2}J_{CF}$ 22.4, $^{3}J_{CF}$ 1.3, $\underline{C}_{Ar}S$), 135.1, (d, $^{2}J_{CF}$ 22.6, $\underline{C}_{Ar}S$), 157.0 (d, $^{1}J_{CF}$ 254.2, $\underline{C}_{Ar}F$), 160.1 (dd, $^{1}J_{CF}$ 240.3, $^{4}J_{CF}$ 2.6, $\underline{C}_{Ar}F$). ^{19}F NMR (CD_3CN, 282.4 MHz): δ_F -105.2 [qd, $^{4}J_{FF}$ 35.5, $^{5}J_{FF}$ 15.1, F-(3)], -95.2 [d, $^{5}J_{FF}$ 15.1, F-(6)], -53.0 (d, $^{4}J_{FF}$ 35.5, 3F, CF_3). Anal. cacld for $C_{13}H_{15}F_5O_3S_3$: C 38.04; H 3.44; F 23.14; S 23.43; *m/z* 410.0098. Found: C 38.07; H 3.44; F 23.11; S 23.58; *m/z* 410.0100.

Acknowledgements

The authors thank the Multi-Access Chemical Research Center of the Siberian Branch of the Russian Academy of Sciences for analytic measurements. The work was financially supported by Russian Science Foundation (grant 16-13-10156)

References

1. Wu, W.; Qin, J.; Li, Z. *Polymer* **2013**, *54*, 4351-4382. http://dx.doi.org/10.1016/j.polymer.2013.05.039.
2. Abd-El-Aziz, A. S.; Strohm, E. A. *Polymer* **2012**, *53*, 4879-4921. http://dx.doi.org/10.1016/j.polymer.2012.08.024.
3. Lee, K.-S.; Kim, R. H.; Yang, D.-Y.; Park, S. H. *Prog. Polym. Sci.* **2008**, *33*, 631-681. http://dx.doi.org/10.1016/j.progpolymsci.2008.01.001.
4. Li, Z.; Wu, W.; Hu, P.; Wu, X.; Yu, G.; Liu, Y.; Ye, C.; Li, Z.; Qin, J. *Dyes Pigm.* **2009**, *81*, 264-272. http://dx.doi.org/10.1016/j.dyepig.2008.10.014.
5. Alijoumaa, K.; Qi, Y.; Ding, J.; Delaire, J. A. *Macromolecules*, **2009**, *42*, 9275-9288. http://dx.doi.org/10.1021/ma900930q.
6. Wu, W.; Huang, Q.; Zhong, C.; Ye, C.; Qin, J.; Li, Z. *Polymer* **2013**, *54*, 5655-5664. http://dx.doi.org/10.1016/j.polymer.2013.07.073.
7. Strehmel, B.; Sarker, A. M.; Detert, H. *ChemPhysChem.* **2003**, *4*, 249-259. https://doi.org/10.1002/cphc.200390041.
8. Siao, Y.-Y.; Shau, S.-M.; Hu, S.-H.; Lee, R.-H.; Lin, C.-H.; Wu, J.-Y.; Jeng, R.-J.*Polymer* **2013**, *54*, 3850-3859. http://dx.doi.org/10.1016/j.polymer.2013.05.040.
9. Sapegin, A.; Krasavin, M. *J. Fluorine Chem.* **2018**, *209*, 56-64. http://dx.doi.org/10.1016/j.jfluchem.2018.02.002.
10. Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem. Int. Ed.* **2003**, *42*, 3900-3903. http://dx.doi.org/10.1002/anie.200351253.
11. Winkler, B.; Meghdadi, F.; Tasch, S.; Müllner, R.; Resel, R.; Saf, R.; Leising, G.; Stelzer, F. *Opt. Mater. (Amsterdam, Neth.)* **1998**, *9*, 159-162. https://doi.org/10.1016/S0925-3467(97)00098-0

12. Tkachenko, I. M.; Belov, N. A.; Kobzar, Y. L.; Dorokhin, A. V.; Shekera, O. V.; Shantarovich, V. P.; Bekeshev, V. G.; Shevchenko, V. V. *J. Fluorine Chem.* **2017**, *195*, 1-12. http://dx.doi.org/10.1016/j.jfluchem.2017.01.008.
13. Park, N. H.; Gomes, G. d. P.; Fevre, M.; Jones, G. O.; Alabugin, I. V.; Hedrick, J. L. *Nature Commun.* **2017**, *8*, Article number: 1553. http://dx.doi.org/10.1038/s41467-017-00186-3.
14. Langner, C.; Meier-Haack, J.; Voit, B.; Komber, H. *J. Fluorine Chem.* **2013**, *156*, 314-321. http://dx.doi.org/10.1016/j.jfluchem.2013.07.013.
15. Amosova, S. V.; Gavrilova, G. M.; Afonin, A. V. *Russ. J. Org. Chem.* **2005**, *41*, 402–405. https://doi.org/10.1007/s11178-005-0178-y.
16. Hynes, R. C.; Peach, M. E. *J. Fluorine Chem.* **1986**, *31*, 129-133. https://doi.org/10.1016/S0022-1139(00)80528-X.
17. Brooke, G. M. *J. Fluorine Chem.* **1997**, *86*, 1-76, and references therein. http://dx.doi.org/10.1016/S0022-1139(97)00006-7
18. Kalhor-Monfared, S.; Jafari, M. R.; Patterson, J. T.; Kitov, P. I.; Dwyer, J. J.; Nuss, J. M.; Derda, R. *Chem. Sci.* **2016**, *7*, 3785-3790 and correction *Chem. Sci.* **2017**, 8, 807. http://dx.doi.org/10.1039/c5sc03856a http://dx.doi.org/10.1039/c6sc90071b
19. Niembo, S.; Vallribera, A.; Moreno-Manas, M. *New J. Chem.* **2008**, *32*, 94-98. http://dx.doi.org/10.1039/b707776a
20. Umemoto, T.; Garrick, L. M.; Saito, N. *Beil. J. Org. Chem.* **2012**, *8*, 461-471. http://dx.doi.org/10.3762/bjoc.8.53
21. Kizner, T. A.; Shteingarts, V. D. *Zh. Org. Khim.* **1989**, *25*, 2424-2431. *Chem. Abstr.* **1990**, *112*, 25, 234891z.
22. Petrucci, R. H., Herring, F. G., Madura, J. D., Bissonnette, C. General Chemistry: Principles and Modern Applications. 10th ed. Pearson Canada Inc., Toronto, Ontario, 2011.
23. Fadeeva, V. P.; Tikhova, V. D.; Nikulicheva, O. N. *J. Anal. Chem.* **2008**, *63*, 1094-1106. https://doi.org/10.1134/S1061934808110142
24. Maksimov, A. M.; Platonov, V. E. *Fluorine Notes* **1999**, *4*, 5-6. http://notes.fluorine1.ru/contents/history/1999/4_1999/letters/index.html

