Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Mesomorphic Properties of Chiral Esters Comprising Partially Fluorinated Alkoxyalkoxy Terminal Chains and a 1-methylheptyl Chiral Moiety

M. Żurowska [a], R. Dąbrowski [a], J. Dziaduszek [a], K. Czupryński [a], K. Skrzypek [a] & M. Filipowicz [a]

[a] Institute of Chemistry, Military University of Technology, Warsaw, Poland

Version of record first published: 30 Jan 2009

To cite this article: M. Żurowska, R. Dąbrowski, J. Dziaduszek, K. Czupryński, K. Skrzypek & M. Filipowicz (2008): Synthesis and Mesomorphic Properties of Chiral Esters Comprising Partially Fluorinated Alkoxyalkoxy Terminal Chains and a 1-methylheptyl Chiral Moiety, Molecular Crystals and Liquid Crystals, 495:1, 145/[497]-157/[509]

To link to this article: http://dx.doi.org/10.1080/15421400802432428

Mol. Cryst. Liq. Cryst., Vol. 495, pp. 145/[497]–157/[509], 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802432428

Taylor & Francis
Taylor & Francis Group

Synthesis and Mesomorphic Properties of Chiral Esters Comprising Partially Fluorinated Alkoxyalkoxy Terminal Chains and a 1-methylheptyl Chiral Moiety

M. Żurowska, R. Dąbrowski, J. Dziaduszek, K. Czupryński, K. Skrzypek, and M. Filipowicz
Institute of Chemistry, Military University of Technology, Warsaw, Poland

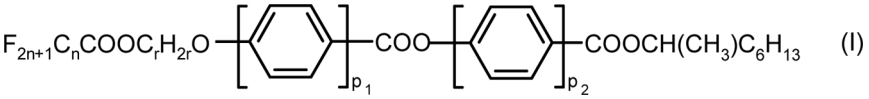
Two structurally similar homologous series of chiral esters with partially fluorinated alkoxyalkoxy terminal chains are described. Their synthetic routes and mesomorphic properties, such as phase transitions temperatures and enthalpies, are characterized by polarizing optical microscope and differential scanning calorimetry.

Keywords: enthalpies; fluorinated AFLCs; phase transitions; synthesis

1. INTRODUCTION

Partially fluorinated three ring esters have high tilted (up to 45°–orthoconic) antiferroelectric phase and show unusual optical properties, which produce perfect dark state and in the consequence high contrast [1]. They are very perspective for many applications.

Many homologous series of esters of general formula (I) with perfluoroalkanoyl unit in the terminal chain have been prepared recently [2–4]



(I)

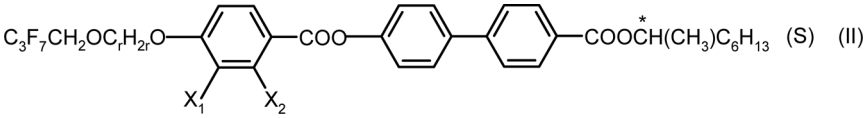
where $p_1 = 1$ and $p_2 = 2$ or $p_1 = 2$ and $p_2 = 1$; $r = 3$–6.

The work was carried under Polish Ministry of Science and Information N204 029 31/0512 support and PBS 765.

Address correspondence to M. Zurowska, Institute of Chemistry, Military University of Technology, Warsaw 00-908, Poland. E-mail: mzurowska@wat.edu.pl

They have low melting point and low melting enthalpy, which enable to formulate orthoconic mixtures existing in a broad temperature range. Unfortunately they have very short helical pitch at room temperature, so well unwounded helical structure is possible to obtain only in very thin cells ($\sim$1 μm) [4]. We are looking for the liquid crystalline materials with longer pitch so the compounds with partially fluorinated alkoxyalkoxy terminal chain are prepared.

The ten compounds expressed by general formula (II)

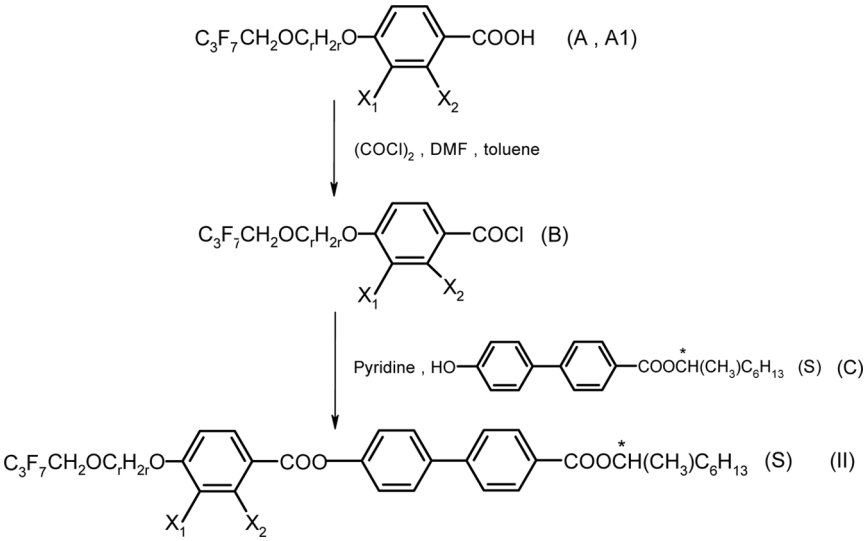


with r = 3, 5, 6, and $X_1 = H$, $X_2 = F$ or $X_1 = F$, $X_2 = H$ or $X_1 = X_2 = H$ or $X_1 = X_2 = F$ are described here.

2. SYNTHESIS

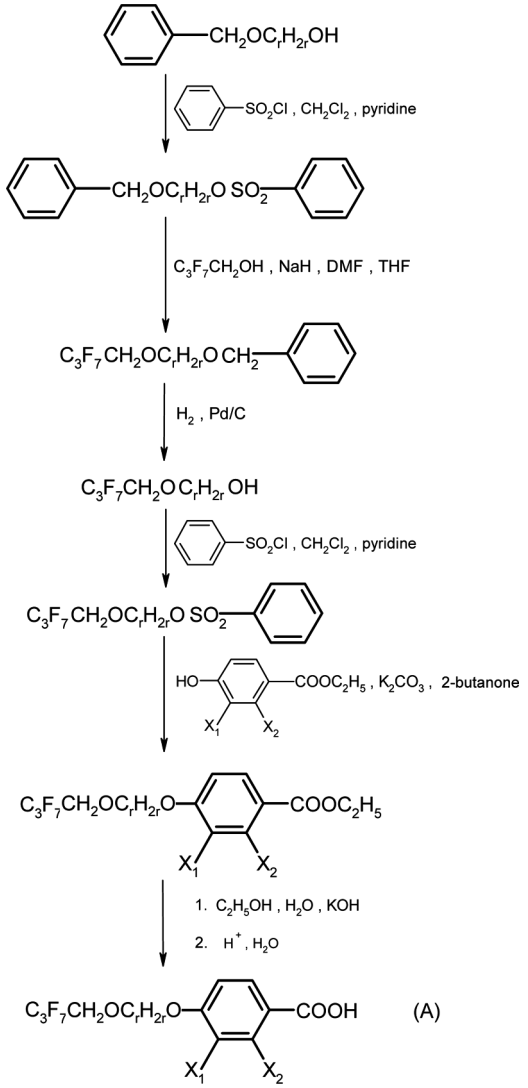
Synthesis of the esters was carried out by treating chiral phenol (C) with benzoic acid chloride (B) [4], see Scheme 1.

The efficient preparation of high optical purity phenol (C) was described recently in Ref. [5].

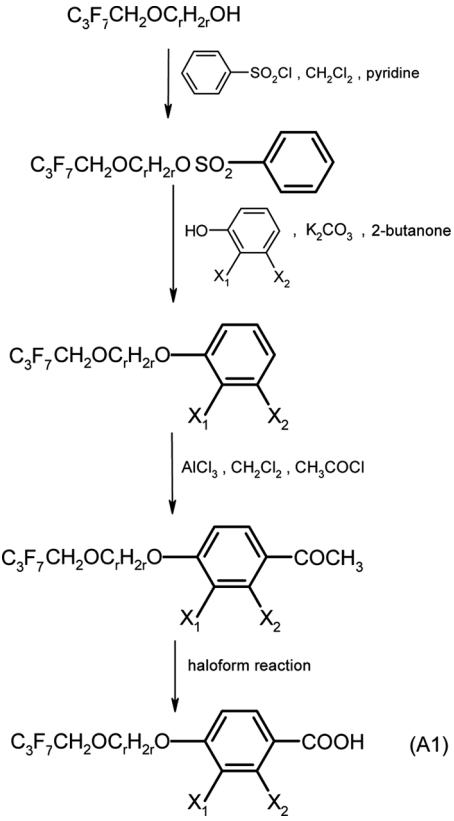


SCHEME 1 Synthetic route of esters with fluoroalkoxyalkoxy chain (II).

The laterally substituted ($X_1 = H$, $X_2 = F$; $X_1 = F$, $X_2 = H$) and unsubstituted ($X_1 = X_2 = H$) fluoroalkoxyalkoxy benzoic acids (A) were prepared using perfluoroalkoxyalkoxy alcohol according to the Scheme 2.



SCHEME 2 Synthetic route of fluoroalkoxyalkoxy benzoic acids with $X_1 = H$, $X_2 = F$; $X_1 = F$, $X_2 = H$; $X_1 = X_2 = H$ (A).



SCHEME 3 Synthetic route of fluoroalkoxyalkoxy benzoic acids with $X_1 = X_2 = F$ (A1).

In case of bilaterally substituted ($X_1 = X_2 = F$) fluoroalkoxyalkoxy benzoic acids (A1) the method shown on Scheme 3 was more convenient.

3. EXPERIMENTAL PART

All reagents were used for reactions as purchased, only toluene was dried by distillation over diphosphorus pentaoxide.

Purity of the liquid crystalline esters was recorded using Schimadzu prominence chromatograph with HPLC MS (API-ESI) detector 2010EV. Purity of the other compounds was checked using Hewlett-Packard HP-6890N chromatograph with MS detector HP5973N.

(S)-(+)-4-hydroxy-4′-(1-methylheptylcarbonyl)biphenyl

m.p.: 86.1°C [5]

1. (S)-(+)-4′-1-methylheptylcarbonyl)biphenyl-4-yl 4-[6-4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2-fluorobenzoate

To the suspension of 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2-fluorobenzoic acid (4.5 g; 10 mmol) in dry toluene (~100 ml), oxalyl chloride (1 ml; 11 mmol) and one drop of N,N-dimethylformamide were added. Vigorous reaction occurs. When the evolution of gases was stopped, mixture was heated at 30°C with stirring for 2 hours. The clear solution was then refluxed and the excess of oxalyl chloride was distilled off with toluene (~25 ml) using Vigreux column. Then (S)-(+)-4-hydroxy-4′-(1-methylheptylcarbonyl)biphenyl (3.26 g; 10 mmol) and pyridine (1.6 ml; 20 mmol) were added to the cold solution. The mixture was stirred at 60°C for 2 days, then it was cooled down to room temperature and poured into the solution prepared from concentrated hydrochloric acid (~2 ml) and water (~200 ml). The layers were separated, the organic layer was washed twice with water. The extract was filtered off by the layer of active carbon. Then it was dried over anhydrous magnesium sulfate and the solvent was evaporated to dryness. The crude-coloured product was crystallized from anhydrous ethanol and acetone (2:1). The obtained solid was purified using column chromatography on silica gel with methylene chloride as eluent. Then ester was recrystallized from anhydrous ethanol and acetone. Yield: 6.2 g; phase transitions of ester are presented in Table 1.

Purity: 98.95%; m.p.: 44.8°C
MS: 769($M + Na^+$), 747($M + H^+$)

The other – nine liquid crystals were obtained in the same way and crystallized from anhydrous ethanol and acetone:

2. (S)-(+)-4′-1-methylheptylcarbonyl)biphenyl-4-yl 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-3-fluorobenzoate

Purity: 99.35%; m.p.: 57.5°C
MS: 769($M + Na^+$), 747($M + H^+$)

TABLE 1 Phase transitions temperatures [°C] and enthalpies [$kJ \cdot mol^{-1}$] of esters 1–10

No	r	X_1	X_2	Cr		SmC^*_{Anti}		SmC^*		SmA		Iso
					44.2–44.8		74.9–75.9		105.4–105.7		105.8–107.1	
1	6	H	F	*	42.2	*	73.9	*	103.7	*	(108.5)	*
					34.2		*0.038*		*4.6*		*2.1*	
					57.5		81.7–83.9		110.4–110.8		114.4–114.9	
2	6	F	H	*	57.3	*	80.1	*	108.5	*	112.7	*
					24.3		*0.017*		*1.15*		*4.4*	
					64.5–65.0		85.0–85.7		112.1–112.5		114.0–114.8	
3	6	F	F	*	62.6	*	84.8	*	110.5	*	112.8	*
					23.2		*0.013*		*0.8*		*3.9*	
					62.0–63.0		95.7–97.0		126.7–126.8		128.2–128.6	
4	6	H	H	*	60.5	*	94.7	*	124.8	*	126.3	*
					24.0		*0.025*		*1.47*		*4.1*	
					–		100.1–100.4		(100.2)		101.0–101.4	
5	5	H	F	*	28.1	*	(97.0)	*	–	*	99.0	*
					34.9		*0.1*		–		*5.4*	
					63.6–64.0		108.8–108.9		108.9–109.0		(111.4–111.6)	
6	5	F	H	*	68.7	*	–	*	106.8	*	109.6	*
					25.4		–		*1.4*		*3.7*	
					–		109.7–110.0		110.2–110.4		111.5–111.8	
7	5	F	F	*	53.5	*	(106.7)	*	107.7	*	109.2	*
					21.6		*0.038*		*1.1*		*3.9*	
					67.3–68.0		123.1–123.6		125.9–126.3			
8	5	H	H	*	66.8	*	121.0	*	123.3	–		*
					18.0		*0.09*		*5.8*			
					51.5–55.3		99.4–100.5					
9	3	F	H	*	51.2	*	98.9	–		–		*
					24.7		*6.0*					
					80.7–81.0		118.0–118.8					
10	3	H	H	*	54.5; 78.9	*	116.2	–		–		*
					3.5; *21.6*		*7.1*					

Upper row – temperature from microscope observations; central row – temperature from DSC observations; down row – enthalpies; ( ) – temperature obtained during cooling cycle.

3. (S)-(+)-4′-(1-methylheptylcarbonyl)biphenyl-4-yl 4- [6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluorobenzoate

Purity: 98.5%; m.p.: 65.0°C
MS: 787($M + Na^+$)

4. (S)-(+)-4′-1-methylheptylcarbonyl)biphenyl-4-yl 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]oxy] benzoate

Purity: 99.9%; m.p.: 63.0°C
MS: 751($M + Na^+$)

5. (S)-(+)-4′-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-2-fluorobenzoate

Purity: 99.9%
MS: 755($M + Na^+$)

6. (S)-(+)-4′-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-3-fluorobenzoate

Purity: 99.4%; m.p.: 64.0°C
MS: 755($M + Na^+$)

7. (S)-(+)-4′-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-2,3-difluorobenzoate

Purity: 98.1%
MS: 773($M + Na^+$)

8. (S)-(+)-4′-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy] benzoate

Purity: 99.7%; m.p.: 68.0°C
MS: 737($M + Na^+$), 715($M + H^+$)

9. (S)-(+)-4′-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[3-(4,4,4,3,3,2,2-heptafluorobutoxy)prop-1-oxy]-3-fluorobenzoate

Purity: 99.9%; m.p.: 55.3°C
MS: 703($M + Na^+$)

10. (S)-(+)-4′-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[3-(4,4,4,3,3,2,2-heptafluorobutoxy)prop-1-oxy] benzoate

Purity: 99.9%; m.p.: 81.0°C
MS: 685($M + Na^+$)

4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hexyl-1] benzenesulfonate

The mixture of 6-(4,4,4,3,3,2,2-heptafluorobutoxy) hexanol-1 (27 g; 90 mmol), pyridine (14.5 ml; 180 mmol) and methylene chloride

(∼160 ml) was cooled down to 0–5°C using acetone and dry ice and benzene sulfonyl chloride (12.7 ml; 99 mmol) was dropped over 2 hours with stirring and cooling to approximately 0°C. The reaction mixture was still stirred at the same temperature for 4 h. Then it was poured into water with crashed ice and stirred for 15 minutes. The organic layer was separated and washed twice with water and ice and twice with diluted hydrochloric acid (∼1%) and again three times with iced water. The organic layer was separated from aqueous layer and dried over anhydrous magnesium sulfate. The solution was filtered through the fluted filter paper to remove the drying medium and the solvent was removed under reduced pressure. The liquid crude product was used to alkylation. Yield: 36.8 g.

4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pentyl-1] benzenesulfonate and 4-[3-(4,4,4,3,3,2,2-heptafluorobutoxy) propyl-1] benzenesulfonate

Obtained the same as 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy] benzenesulfonate.

ethyl 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2-flurobenzoate

4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hexyl-1] benzenesulfonate (36.8 g; 84 mmol), ethyl 4-hydroxy-2-fluorobenzoate (15.5 g; 84 mmol), potassium carbonate (23.2 g; 168 mmol) and 2-butanone (∼150 ml) were refluxed with stirring for 2 days. The mixture was cooled down and poured into water (∼2 l) and stirred for 3 hours. The solution was extracted three times with methylene chloride. The combined organic layers were washed twice with water and separated using separator funnel. Then the organic layer was filtered through an active carbon and dried over anhydrous magnesium sulfate. The solvent was removed on the rotary evaporator. The crude product was used to hydrolysis. Yield: 37.2 g.

Purity: 99.4%
MS: 466(M+), 421, 213, 184, 156, 139, 83, 55, 29

The other esters were obtained the same as ethyl 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy] 2-fluorobenzoate:

ethyl 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-3-flurobenzoate

Purity: 96.8%
MS: 466(M+), 213, 184, 156, 139, 83, 55, 29

ethyl 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy] benzoate

Purity: 88.1%
MS: 448(M+), 403, 213, 166, 138, 83, 55

ethyl 4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-2-fluorobenzoate

Purity: 93.0%
MS: 452(M+), 213, 139, 69, 41

ethyl 4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-3-fluorobenzoate

Purity: 89.0%
MS: 452(M+), 407, 269, 213, 184, 156, 69, 41

ethyl 4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy] benzoate

Purity: 87.9%
MS: 434(M+), 389, 269, 213, 166, 138, 69, 41

ethyl 4-[3-(4,4,4,3,3,2,2-heptafluorobutoxy)prop-1-oxy]-3-fluorobenzoate and ethyl 4-[3-(4,4,4,3,3,2,2-heptafluorobutoxy)prop-1-oxy]benzoate4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2-fluorobenzoic acid

Ethyl 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2-fluorobenzoate (37.2 g; 79 mmol), potassium hydroxide (11.2 g; 200 mmol), ethanol (~100 ml) and water (~10 ml) were refluxed with stirring for 4 hours. The progress of reaction was monitored by TLC. Then the reaction mixture was cooled down, poured into water (~800 ml), acidified with concentrated hydrochloric acid (~20 ml) and stirred for 2 hours; pH of solution was checked by indicator paper. The formed precipitate was collected by filtration, washed with water and crystallized from ethanol and water (~2:1). Yield: 28.6 g.

Purity: 97.8%
MS: 438(M+), 213, 156, 139, 83, 55, 41, 29

The other acids were obtained the same as 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2-fluorobenzoic acid and crystallized from ethanol and water.

4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy] 3-fluorobenzoic acid

Purity: 99.9%
MS: 438(M+), 213, 156, 139, 83, 55, 41, 29

4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy] benzoic acid

Purity: 99.8%

4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-2-fluorobenzoic acid

Purity: 99.5%

4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-3-fluorobenzoic acid

Purity: 99.9%

4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy] benzoic acid

Purity: 99.8%

4-[3-(4,4,4,3,3,2,2-heptafluorobutoxy)prop-1-oxy]-3-fluorobenzoic acid

Purity: 99.9%

4-[3-(4,4,4,3,3,2,2-heptafluorobutoxy)prop-1-oxy] benzoic acid

Purity: 98.8%

4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluorobenzene

4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hexyl-1]benzenesulfonate (112.8 g; 256 mmol), 4-hydroxy-2,3-difluorobenzene (27.7 g; 213 mmol), potassium carbonate (58.7 g; 426 mmol) and 2-butanone (∼600 refluxed with stirring for 10 hours. The mixture was cooled down and poured into water (∼2000 stirred for 3 hours. The solution was extracted three times with methylene chloride. The combined organic layers were washed twice with water and separated. Then the organic layer was filtered through an active carbon and dried over anhydrous

magnesium sulfate. The solvent was removed on the rotary evaporator. The liquid product was purified using vacuum distillation. The product was used to acylation. Yield: 67.9 g.

Purity: 93.3%
MS: 412(M+), 213, 130, 83, 55, 29

4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-2,3-difluorobenzene

Obtained the same as 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluorobenzene.

Purity: 91.9%
MS: 398(M+), 269, 213, 130, 69, 41

4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluoroacetophenone

Acyl chloride (17 ml; 240 mmol) was dropped slowly to the stirred mixture of aluminium chloride (30.8 g; 231 mmol) and dry methylene chloride (~200 ml). When the homogeneous solution was prepared, the mixture was cooled down to 0–5°C and 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluorobenzene (67.9 g; 165 mmol) was added dropwise over a period of 1 hour. After dropping was completed the mixture was stirred at 0–5°C for 4 hours. Then it was poured into water with crashed ice and stirred. The layers were separated, the organic layer was washed three times with water, then the solution was transferred to the separatory funnel, extracted with methylene chloride and separated precisely. The extract was dried over anhydrous magnesium sulfate and the solvent was removed using the rotary evaporator. The liquid product was distilled using vacuum. The product was used to haloform reaction without further purification. Yield: 51.5 g.

Purity: 80.2%
MS: 454(M+), 213, 157, 83, 55, 29

4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-2,3-difluoroacetophenone

Obtained the same as 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluoroacetophenone.

Purity: 89.8%
MS: 440(M+), 269, 213, 172, 157, 69, 41

4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluorobenzoic acid

To the stirred hypobromite solution prepared from sodium hydroxide water solution (72.3 g in 68 ml of water), crushed ice (226 g) and bromine (72.3 g; 23.2 ml), 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluoroacetophenone dissolved in 300 ml of 1,4-dioxane was added in one portion. The temperature was increased to 25°C very quickly, because the exothermic reaction occurs. When the temperature started to decrease, the further reaction was initiated by gentle heating on the water bath. When the reaction stopped, a new solution of hypobromite prepared the same and 200 ml of 1,4-dioxane were added to the reaction mixture. The temperature was increased to about 25°C once again. The colour of the stirred reaction mixture was turned light. Then the mixture was heated at about 60°C for 2 hours using water bath. After that it was cooled down to the room temperature, discoloured using sodium pyrosulfite, poured into water with hydrochloric acid and stirred for 2 hours; pH of solution was checked by indicator paper. The precipitate was formed and it was filtered through the filter paper and washed with plenty of water. The solid product was crystallized from methanol. Yield: 31.0 g.

4-[5-(4,4,4,3,3,2,2-heptafluorobutoxy)pent-1-oxy]-2,3-difluorobenzoic acid

Obtained the same as 4-[6-(4,4,4,3,3,2,2-heptafluorobutoxy)hex-1-oxy]-2,3-difluorobenzoic acid. Crystallization from methanol.

4. MESOMORPHISM OF PREPARED COMPOUNDS

The sequence of phases and phase transitions temperatures of the liquid crystals were measured by texture observation in "Biolar" polarizing microscope (PZO) equipped with "Linkam" TMS-93 hot stage. The temperatures of phase transitions and enthalpies were recorded by DSC "Setaram" 141 microcalorimeter in heating and cooling cycles. The results of measurements in heating cycle are listed below in the Table 1.

The all compounds have anticlinic smectic phase (SmC^*_{Anti}) in a broad temperature range and synclinic smectic phase (SmC^*) and orthogonal smectic phase (SmA) above it in short temperature range, see the Table 1. Temperature range of SmC^* phase and SmA phase is smaller in series r = 5 than in series r = 6. In case of compound 8 the

SmA phase disappeares totally. For the compounds with $r = 3$ the direct phase transition SmC^*_{Anti} – Iso was observed [4].

5. CONCLUSIONS

The compounds with partially fluorinated alkoxyalkoxy terminal chain have antiferroelectric phase in a broad temperature range similar to the compounds with partially fluorinated alkanoyloxyalkoxy chain. Longer methylene spacer promotes the presence ferroelectric phase (SmC^*).

REFERENCES

[1] Lagerwall, S., Dahlgren, A., Jagemal, P., Rudquist, P., D'have, K., Pauwels, H., Dąbrowski, R., & Drzewiński, W. (2001). *Adv. Funct. Mater*, *11*, 87–94.
[2] Dąbrowski, R., Gąsowska, J., Otón, J. M., Piecek, W., Przedmojski, J., & Tykarska, M. (2004). *Displays*, *25*, 9–19.
[3] Gąsowska, J., Dąbrowski, R., Drzewiński, W., Filipowicz, M., Przedmojski, J., & Kenig, K. (2004). *Ferroelectrics*, *309*, 83–93.
[4] Sokół, E., Drzewiński, W., Dziaduszek, J., Dąbrowski, R., Bennis, N., & Otón, J. M. (2006). *Ferroelectrics*, *343*, 41–48.
[5] Drzewiński, W., Dąbrowski R., & Czupryński, K. (2002). *Polish J. Chem.*, *76*, 273–284.