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Orthoconic Antiferroelectrics. Synthesis and Mesomorphic Properties of Optically Active (S)-(+)-4-(1-Methylheptyloxycarbonyl)phenyl 4′-(fluoroalkanoyloxyalkoxy)biphenyl-4-carboxylates and 4′-(Alkanoyloxyalkoxy)biphenyl-4-carboxylates*

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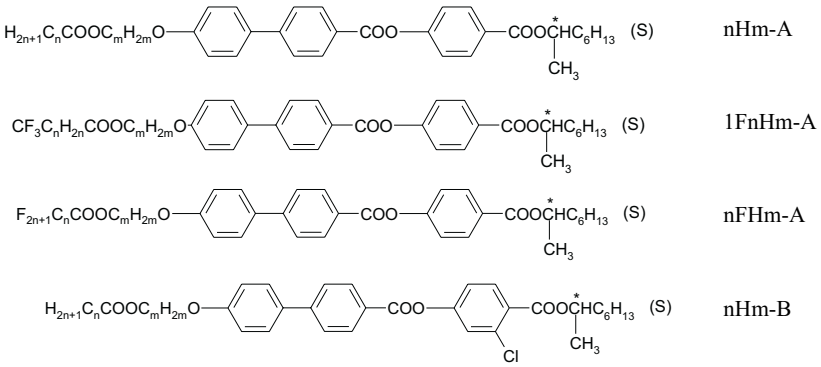
Convenient methods for preparing optically active (S)-(+)-4-(1-methylheptyloxy-carbonyl)-phenyl 4′-(ω-perfluoroalkanoyloxyalkoxy)- and 4′-(ω-alkanoyloxy-alkoxy)biphenyl-4-carboxylates and their intermediates have been described and discussed. The phase transitions of the prepared esters have been investigated by differential scanning calorimetry.

Key words: anticlinic smectics, synthesis of chiral orthoconic esters, phase transitions, DSC

Antiferroelectric materials have been intensively studied during the last decade [1,2], because of their applications especially in flat-panel displays. They offer a better gray scale and a simpler driving scheme than ferroelectric ones. In spite of these advantages commercial production of antiferroelectric liquid crystal (AFLC) displays have not been started yet, because of some technological problems related to the small value of contrast ratio. Recently, we started investigations of three ring esters having an alkanoyloxyalkoxy or perfluoroalkanoyloxyalkoxy terminal chain [3,4] and have found that the second ester family had the smectic layers with anticlinic order and a very high tilt [5]. Thus, smectic mixtures having layers tilted at 45 degree were obtained [6]. They were the first AFLC mixtures with such properties. The materials were called orthoconic antiferroelectrics, because their tilt direction alternates from layer to layer by 90 degrees. These new materials have also been investigated in Lagerwall's laboratory [6–9]. There has been found, that their optical properties are unique among liquid crystals, what enables to obtain an excellent dark state, solving the contrast problem [8]. Normal surface stabilized-antiferroelectrics are optically biaxial positive liquid crystals, with the effective optic axes along the smectic layer, while the orthoconic antiferroelectrics are optically uniaxial negative liquid crystals. In the antiferroelectric state the orthoconic antiferroelectric behaves

*Dedicated to the memory of Professor Krzysztof Pigoń.

as an isotropic medium [8,9] and surface defects are not seen, what generates the excellent dark state. It seems, that these materials are the most perspective for present and future applications among the known liquid crystalline antiferroelectrics and therefore their further development is necessary. Laboratories have started to synthesize them [10] and an interdisciplinary scientific net for studies of the similar materials under 5th European Framework was established [11]. In [4] we showed a scheme for the syntheses of perfluoroalkanoyloxyalkoxybiphenylates without experimental details. Meanwhile, we have improved the experimental procedure (synthesis and purification) and now high purity compounds more effectively and economically may be prepared. It is described in the experimental part. The phase transitions of the all prepared until now esters belonging to four homologous series of the four following structures are also described.

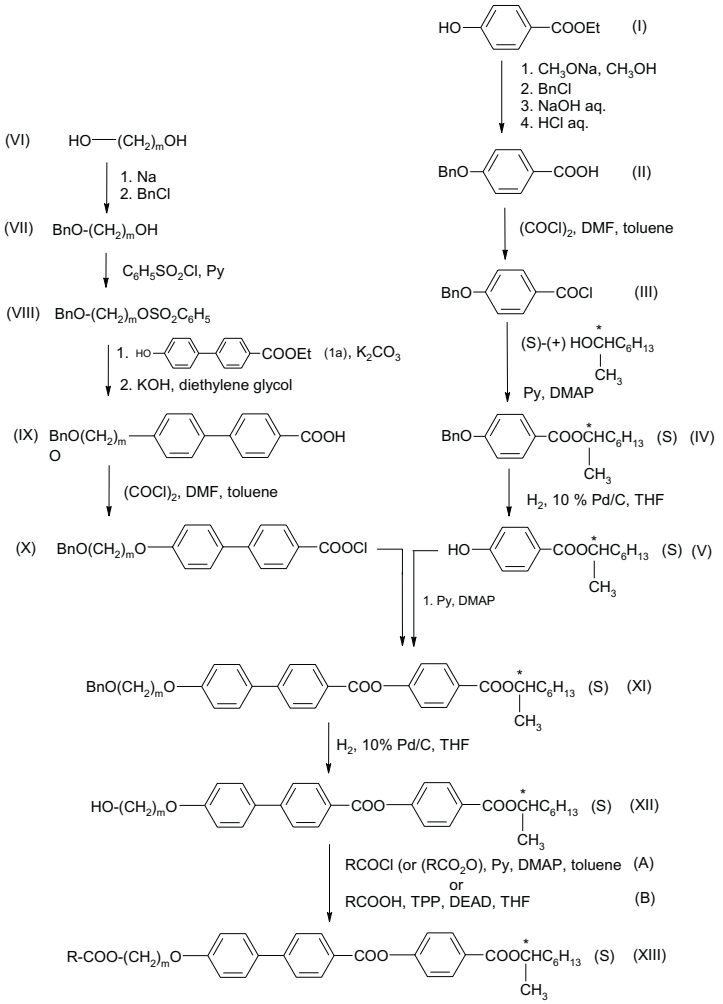


A and B express the fixed part of ester molecules and nHm, 1FnHm or nFHm variable tails.

RESULTS AND DISCUSSION

Synthesis: The elaborated and recommended synthesis route for the esters of nHm-A, 1FnHm, nFHm-A, and nHm-B series is shown in Scheme 1 and the preparative details of the method are described in the experimental part. It is a still time consuming procedure, due to the multistep reaction and the necessity of the protection and deprotection of the hydroxyl group to conduct reactions in the desired direction and to avoid side reactions. Benzyl group was used for the protection, because it is easily and quantitatively removed by gaseous hydrogen in the presence of a palladium catalyst on active carbon and the debenzylated product does not need purification. Perfluoroalkanecarboxylic acids and optically active (S)-(+) octanol-2 are the most expensive reactants. Therefore, it is better if they are used as late as possible. As it appears from Scheme 1 unit A (or B), the same as in the final the antiferroelectric molecules XIII, is formed in the reaction of esterification from S-(+)-1-(1-methylheptyl) 4-hydroxybenzoate (V) (or (S)-(+)-1-methylheptyl 3-chloro-4-hydroxybenzoate) and 4-(ω-benzyloxyalkoxy)biphenyl-carboxylic acid chloride (X), while

previously (S)-(+)-1-(1-methylheptyl) 4-hydroxybenzoate (V) was transformed to the desired (S)-(+)-4-(1-methylheptyloxycarbonyl)phenyl 4-(ω-hydroxyalkoxy)biphenylcarboxylates (XI) *via* (S)-(+)-4-(1-methylheptyloxycarbonyl)phenyl 4-hydroxybiphenylcarboxylate, thus the consumption of optically active reactant V is lower now. In both procedures the alkanoyloxy group is placed in the last stage, what ensures a high yield referred also to the fluorinated reactant as well as the high purity of the product. The perfluorocarbonyloxy group is very unstable, because it is highly susceptible to a nucleophilic attack and would be removed during the next stages if it were introduced early. The esters of series nFHm are especially unstable in alkaline medium and they are quickly decomposed on aluminum oxide, which is commonly used for the purification of liquid crystals.



Scheme 1. Synthesis route of alkanoyloxyalkoxybiphenylcarboxylates of series nHm-A, 1FnHm-A, nFHm-A, nHm-B; where R = C_nH_{2n+1} – nHm-A and nHm-B; $CF_3C_nH_{2n}$ – 1FnHm-A; C_nF_{2n+1} – nFHm-A.

Usually aromatic liquid crystalline esters are prepared by a reaction between carboxylic acid and phenol in the presence of DCC-DMAP [12]. We have found that the use of acid chloride and pyridine as the catalyst gave the product (XI) easier in purification than that obtained from free acid, because in the case of the high molecular esters the removing of dicyclohexylurea and N-acyl-dicyclohexylourea arised from DCC is a problem. The esterification with chlorides was also a very efficient reaction in the case of final product XIII and chiral benzyloxyester (IV). In order to achieve ester IV, the esterification was carried at in an excess (5–7 fold) pyridine together with a very small catalytic amount of dimethylaminopyridine (DMAP). In these conditions a very high optical purity and the retention of absolute (S) configuration were obtained. The optical rotation coefficient of ester IV was $[\alpha_D^{20}] = +40.7°$, while the value given in [13] was $[\alpha_D^{23.4}] = +27.4°$. In the last case the esterification was made by Mitsunobu method [14], which needs (R)-(–)-octanol-2 and free acid, because a stereogenic inversion process occurs there. We also used the compound V for preparation of MHPOBC, which was the first investigated and is until now the best known antiferroelectric compound to confirm that our procedure gives a product with good optical quality. We found that our product had also three subphases above SmC_A^* phase with the transitions very well seen by the DSC method, as it was in the case of MHPOBC but they appeared in another sequence than previously reported [1]. The subphases observed during cooling were: SmC_α-$SmC_{\gamma 2}$-$SmC_{\gamma 1}$ ($SmC_{\gamma 2}$ is marked also as AF) [15]. Doping the compound by the second R enantiomer gave the usually observed sequence of the subphases: SmC_α-SmC_β (normal synclinic smectic C^*)-$SmC_{\gamma 1}$-SmC_A^* [15]. Treating of the compound XII with acid chlorides produced the final esters XIII. In the case of fluorinated esters 1FnHm and nFHm also acid anhydrides or free acids were used. In the latter case Mitsunobu condition was adopted (for esterification). It resulted from the attainability of the reactants. Only perfluorobutanoic acid chloride is commercially available and also anhydrides with n = 1, 2. The preparation of a small amount of higher perfluoroacid chlorides from free acids is not economical in laboratory conditions, because they separate with difficulty from a chlorinating agent. Therefore, in those cases the esters were prepared in Mitsunobu condition (TPP, DEAD). The yield was quite satisfying, 70%. The high purity of compounds (the absence of ionic or dissociating impurities) is crucial for testing the electrooptical properties and their applications. For these reasons the final esters XIII were purificated very carefully. A chromatographic thermostated column, silicagel as a sorbent and heptane as an eluant were used. Under these conditions the polar impurities (phenols and acids) were kept in the column and the nearly pure ester was eluated. Then the product was crystallized several times from ethanol, until one spot on TLC plates was observed. The silicagel chromatographic plates and aluminum oxide plates (the last only in the case of protonated esters) and two eluant systems: pure $CHCl_3$ or $CHCl_3$-hexane (9:1) mixture were used. The obtained compounds were of a very high chemical purity, higher than 99.9%. It was also confirmed by sharp phase transitions, established by DSC, see example in Figure 1. The recent temperature

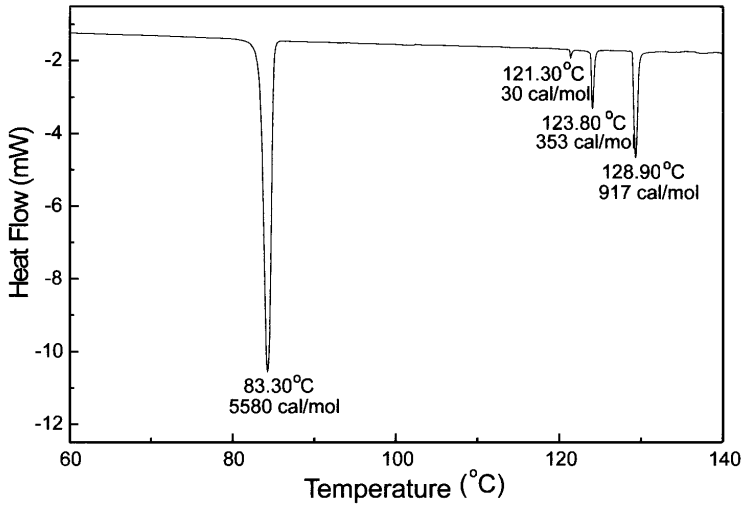
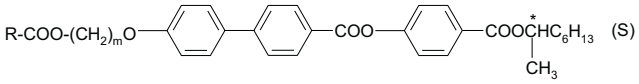


Figure 1. The DSC trace of 3FH3-A compound.

measurements of the tilt angle, spontaneous polarization, density, also gave sharp drops of values during the transitions [16].

Phase transitions: The phase transition temperatures of members from homologous series nHm-A, 1FnHm-A, nFHm-A and nHm-B are listed in Table 1. A part of them was reported previously [4], but their synthesis was also repeated in few cases and the phase transitions of the all compounds were measured again by very precise differential scanning calorimeter SETARAM 141. In homologous series nHm-A with the fixed m = 3 a phase sequence Iso-SmA-SmC^*_A-SmI^*_A is observed for values n = 1–5 and for n ≥ 6 a smectic C^* phase appears in a small temperature range. The smectic I^*_A phase is not observed for the members with fixed m = 4 and the synclinic smectic C^* phase is much earlier observed here, already from n = 3. The melting enthalpy of those compounds, which is an important parameter for mixture formulations is lower in the members with m = 3 than in members with m = 4. The introduction of CF_3 group in the terminal position of the chain (compounds 1FH3-A, 1F2H3-A, 1F2H4-A) promotes the presence of the synclinic smectic C^* phase and increases the transition temperatures between all smectic phases except SmI^*_A phase, which disappears. The melting point and the melting enthalpy also increase but the last feature is not desired. The exchange of the alkanoyloxy unit by perfluoroalkanoyloxy one increases the stability of tilted phases: SmC^*_A and SmC^*. In series nFHm-A the smectic C^*_A phase is more stable for shorter fluorinated chain than for longer fluorinated one (compare compounds 1FH3-A and 7FH3-A). The phase sequence Iso-SmA-SmC^*-SmC^*_A appears for a very short perfluoroalkyl fragment, that is observed since n = 1. It is quite unusual behavior because tilted phases are characteristic of compounds with longer tails. The melting enthalpy is not high, so eutectic mixtures with a low melting point may be formulated. The introduction of a chlorine atom in the orto-position to the chiral ester bond decreases all phase transitions temperatures, also the melting point and the both tilted smectic phases. The synclinic SmC^*_β as well as anticlinic SmC^*_A are saved.

Table 1. Temperatures /°C – first row and enthalpies/kcal/mol – second row of phase transitions as obtained from DSC measurements.

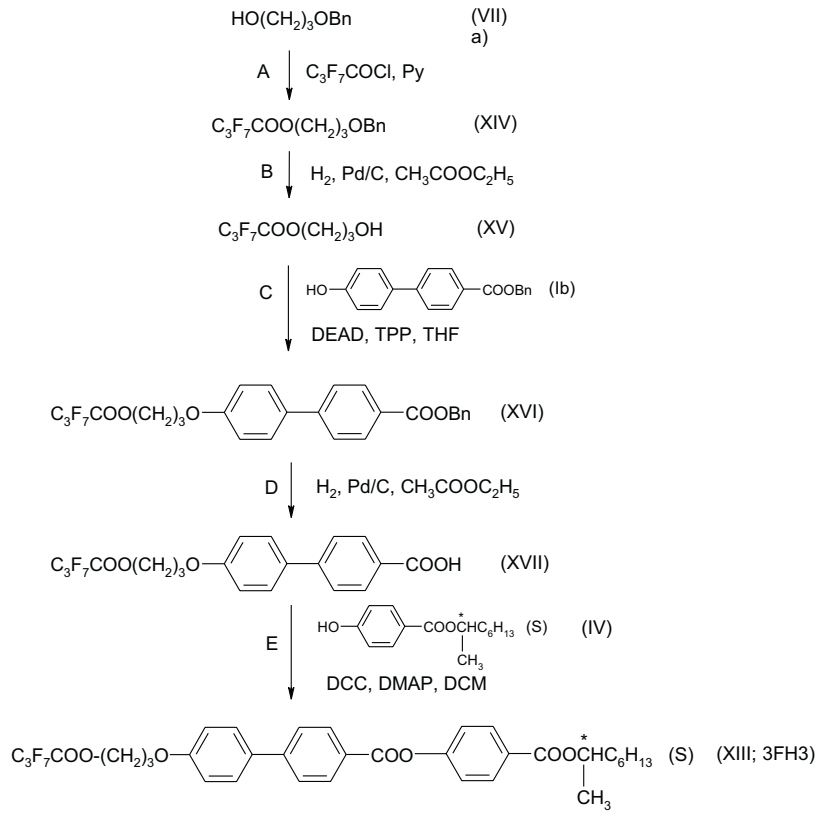


R = $H_{2n+1}C_n$ – series nHm-A and nHm-B; $CF_3(CH_2)_n$ – series 1FnHm-A;- $F_{2n+1}C_n$ – series nFHm–A

	n	m	Acronym	Cr_1		Cr		I^*_A		C^*_A		C^*_β		A		I
1.	1	3	1H3-A	*	57.5 *1.37*	*	62.6 *2.15*	(*	52.7) *0.08*	–		–		*	129.7 *1.32*	*
2.	1	3	1FH3-A	*	74.4 *0.56*	*	81.0 *4.32*	–		*	122.0 *0.02*	*	125.9 *0.14*	*	130.9 *1.18*	*
3.	2	3	2H3-A	–		*	77.3 *5.69*	(*	49.2) *0.10*	*	88.2 *0.013*	–		*	123.6 *1.29*	*
4.	2	3	2FH3-A	–		*	103.7 *6.09*	(*	45.0) *0.10*	*	120.6 *0.05*	*	122.3 *0.26*	*	125.4 *0.96*	*
5.	3	3	3H3-A	–		*	66.6 *5.33*	(*	43.0) *0.3*	*	92.4 *0.02*	–		*	117.3 *1.22*	*
6.	3	3	3FH3-A	–		*	83.3 *5.58*	(*	54.0) *0.10*	*	121.3 *0.03*	*	123.8 *0.35*	*	128.9 *0.92*	*
7.	3	4	3H4-B	–		*	55.1 *7.80*	–		*	68.5 *0.05*	*	69.1 *0.14*	*	71.5 *0.69*	
8.	3	4	3H4-A	–		*	71.0 *9.74*	–		*	92.4 *0.01*	*	100.5 *0.08*	*	110.0 *1.04*	*
9.	2	3	1F2H3-A	–		*	99.0 *7.34*	–		*	111.0 *0.012*	*	122.5 *0.12*	*	126.9 *1.36*	*
10.	3	4	3FH4-A	–		*	68.4 *3.86*	–		*	120.1 *0.02*	*	126.6 *0.47*	*	127.0 *0.79*	*
11.	3	5	3FH5-A	*	52.8 *1.94*	*	65.8 *4.65*	–		*	122.5 *0.02*	*	124.2 *0.27*	*	132.8 *0.76*	*
12.	2	4	1F2H4-A	–		*	88.4 *10.37*	–		*	112.4 *0.02*	*	115.2 *0.21*	*	116.9 *1.03*	*
13.	4	3	4H3-A	–		*	62.2 *5.28*	(*	31.9) *0.12*	*	92.8 *0.06*	–		*	111.7 *1.28*	*
14.	4	3	4FH3-A	–		*	72.0 *5.46*	–		*	114.9 *0.015*	*	123.7 *0.33*	*	134.4 *0.97*	*
15.	4	5	4FH5-A	–		*	60.5 *9.57*	–		*	117.6 *0.015*	*	123.7 *0.27*	*	136.9 *0.75*	*
16.	5	3	5H3-A	–		*	73.6 *8.56*	(*	26.3) *0.24*	*	92.5 *0.07*	–		*	109.1 *1.26*	*
17.	5	4	5H4-A	–		*	72.6 *9.72*	–		*	93.1 *0.01*	*	97.0 *0.09*	*	104.0 *1.07*	*
18.	6	3	6H3-A	–	51.6 *1.74*	*	69.2 *8.17*	(*	22.0) *0.19*	*	91.0 *0.03*	*	92.2 *0.05*	*	106.6 *1.29*	*
19.	7	3	7H3-A	–		*	49.5 *8.11*	(*	25.0) *0.10*	*	89.9 *0.02*	*	91.9 *0.05*	*	105.4 *1.38*	*
20.	7	3	7FH3-A	–		*	68.6 *5.02*	–		*	97.5 *0.005*	*	124.3 *0.17*	*	153.5 *1.22*	*
21.	7	4	7H4-A	–		*	79.7 *11.20*	–		*	90.8 *0.01*	*	93.9 *0.09*	*	100.7 *1.15*	*

( ) – value in parentheses – monotropic transition (observed only during cooling cycle).

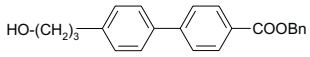
Discussion: We found that the route of synthesis shown in Scheme 1 was economical and ensured the products of high purity, although for the effective removing of polar contaminations, purification on the chromatographic column followed by crystallization should be performed. Recently Hird *et al*. [10] have started to synthesize the orthoconic antiferroelectic and the compound 3FH3-A was obtained in the way shown in Scheme 2.



Scheme 2. Synthesis route of compound XIII proposed in [10] and tested on the example of compound 3FH3-A.

Their product had the following phase transitions: Cr 83.5 SmC^*_A 136.5 SmC^*_β 139.0 SmA 152.0 Iso. They did not observe SmI^*_A phase and the transitions SmC^*_A-SmC^*_β-SmA-Iso were much higher than reported by us in [4]. We reported the transitions: Cr 83.5 (SmI_A 54) SmC^*_A 121.0 SmC^*_β 123.6 SmA 128.8 Iso. This compound obtained again and carefully purificated in the manner described here (it contained impurity in amount less than 0.1%) had the transitions: Cr 83.3 (SmI_A 54) SmC^*_A 121.3 SmC^*_β 123.8 SmA 128.9 Iso.

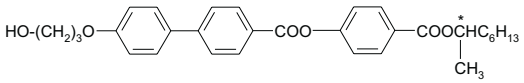
We have repeated also the route of the synthesis shown in Scheme 2 and found that the intermediate product XVI arised with a very small yield. The ester bond C_3F_7COO-$(CH_2)_3$- was broken and the compound XVIII:



(XVIII)

was mainly produced.

Inventors of the method [10] also reported the low yield of this step. Then we found that the final product XIII formed in the esterification reaction in the presence of DCC is strongly contaminated by hydroxyester (XII):



(XII)

because further destroying of the ester bond was accompanying the reaction. Hydroxyester (XII) has the phase transition: Cr 140 SmA 167 Iso.

The phase transition temperatures in the hydroxyester XII are much higher than those for ester 3FH3-A. Probably presence of this compound and 4-(3-heptafluorobunatoyloxyprop-1-oxy)-biphenyl-4′-carboxylic acid as the impurities in the ester described in [10] are responsible for the observed higher temperatures of the transitions. We doped the ester 3FH3-A by 5% of XII and found the following phase transitions: Cr 74.5 SmC^*_A 124.2 SmC 126.7 SmA 134 Iso. Therefore, the transition values given in [10] are not rather mutual property of the compound 3FH3-A. The correct values are as listed in Table 1.

According to our results, the synthesis *via* route shown in Scheme 2 does not seem to be effective, especially in the case of the preparation of esters with the $C_nF_{2n+1}COO(CH_2)_mO$- terminal tail, because not only the yield is small but also the product is not pure. The method given in Scheme 1, in which the perfluoroalkanoyloxy group is formed at the end stage of the synthesis, yields much better results.

The exchange of the alkanoyloxy group by its fully fluorinated analogue influences very positively the properties of the anticlinic smectic compounds – important for mixture formulations and applications.

The measurements of their physical parameters in the parallel works [5–9,16–17] showed that not only phase transition temperatures, phase sequence and enthalpy described here, but also other physical parameters differ significantly from the protonated analogues. Fluorination promotes the high tilted order. It is probably a consequence of another molecular packing in the smectic layers. The high tilt arises rapidly in fluorinated compounds during the transition to the tilted layer structure [5,16] and then the tilt is growing slowly. Such substances are characterized by a very desired property – the high tilt and the small temperature dependence of the tilt. Spontaneous polarization grows simultaneously to a high value and it changes with temperature in a similar way as the tilt [5,16]. In protonated analogues nHm-A the tilt and the spontaneous polarization are much lower and they change monotonically with the increase of temperature.

The compounds of series nFHm-A have higher density than nHm-A and their smectic layers are thinner also in SmA phase although the molecules are a slightly

longer [17]. In spite of this the relaxation process connected with reorientation around the short axis in smectic C^*_A phase has lower activation enthalpy for fluorinated nFHm-A members than protonated nHm-A ones [5].

They have a low or moderate melting point enthalpy and the length of the chain does not influence strongly the observed values, therefore, the compounds with short as well with long tails may be useful. This increases the probability of finding the optimum candidates for formulation of eutectic compositions with a strong depressing of the melting points. The transition from the orthogonal smectic A phase to the tilted SmC^* phase in the fluorinated members of series nHFm-A is a first order transition and is stronger than the one observed in the protonated members of series nHm-A. Also the phase sequence is convenient, because it follows Iso-SmA-SmC^*-SmC^*_A. The tilted phases exist in a large temperature interval, what promotes the small dependence of the tilt upon temperature and in the consequence, the small temperature dependence of the physical parameters correlated with the tilt.

The physical properties discussed above showed that the fluorinated antiferroelectrics are quite different from the protonated antiferroelectrics. They seem extremely interesting not only from the material science point of view but also for applications. Searching the other classes of compounds with similar properties and developing and improving methods of their synthesis seems to be one of the main tasks in chemistry of liquid crystals now.

EXPERIMENTAL

The structures of intermediates and products were confirmed by mass spectrometry (Hewlett Packard mass detector HP 5972) and infrared spectroscopy (Fourier infrared spectrometer BIO-RAD FTS75C) and in some cases by combustion data. Transition temperatures were tested using DSC (SETARAM 141) and polarizing microscope (Biolar-PZO connected with Linkam THMS-600 heating stage). The observed phases were confirmed by the miscibility method, microscopy patterns and X-ray diffraction patterns.

The purity was tested by gas chromatography (Hewlett-Packard HP-5890 equipped with FID detector, capillary column type ultra-2, 30 m length and 0.3 mm diameter were used; 20 m and 0.3 mm in case of the MS detector and by thin layer chromatography (silicagel plates and aluminum oxide plates), a specific rotation coefficient was measured by a polarimetric method, polarimeter B&L model A (10 cm length and 8 mm diameter tubes). (S)-(+) 2-octanol "chiral select" – purity e.e > 99% from Fluka and fluorinated chemicals from "ABCR" were used.

4-Benzyloxybenzoic acid (II): To the solution of sodium methoxide (54.0 g; 1 mole) in methanol (1.0 l) ethyl 4-hydroxy-benzoate (166.0 g; 1 mole) was added in one portion and then benzyl chloride (120.0 g; 0.95 mole) was dropped under reflux. The refluxing was continued for six hours and then sodium hydroxide (80.0 g; 2.0 mole) dissolved in 250 ml of water was dropped. The mixture was refluxed for eight hours and poured into 2 l of water containing 250 ml of concentrated hydrochloric acid. The solid product was filtered, washed carefully with cold water and methanol and then crystallized from ethanol (2 l) and then from toluene (1.5 l). 4-Benzyloxybenzoic acid was obtained as white crystals; yield 189.2 g (83%); m.p. 192–193.5°C, Ref. [18] (m.p. 187–190).

By the same method 4-benzyloxy-2-chlorobenzoic acid was obtained; m.p. Cr_1 120 Cr 142-144 Iso.

(S)-(+)-1-Methylheptyl 4-benzyloxybenzoate (IV): To the mixture of benzyloxybenzoic acid (II) (22.8 g; 0.1 mole), toluene (150 ml) and oxalyl chloride (24.5 g; 0.2 mole) two drops of N,N-dimethylformamide were added and the mixture was heated on water bath (40–45°C) until dissolving of

the acid. Then excess of oxalyl chloride was distilled off through 20 cm Vigreux column with a small amount of toluene. The solution of acyl chloride was cooled to the room temperature and diluted with toluene to the total volume 200 ml and pyridine (16.0 ml; 0.2 mole) was added in one portion. After 0.5 h (S)-(+)-2-octanol (13.0 g; 0.1 mole) was dropped through ~30 min. Temperature was raised to 35°C spontaneously. When the exothermic effect failed, the mixture was heated on water bath to 40–45°C for 16 h. Then it was poured onto water with ice (~250 ml) and acidified with concentrated hydrochloric acid (20 ml). Organic layer was separated, washed with 5% hydrochloric acid (2×100 ml), water (2×100 ml), brine (100 ml) and then dried over anhydrous magnesium sulphate. The dry solution was filtered, drying agent was washed with small amount of toluene and solvent was evaporated. The crude product was dissolved at hexane (500 ml) and passed through Fuller earth layer and then silica gel column (3 cm diameter and 10 cm length). The solvent was evaporated carefully and obtained oil was crystallized from methanol (300 ml). Yield 30.9 g (91%), purity 99.9% (GC); m.p. 24–24.5°C; $\alpha_D^{20} = +35.2^o$ (c = 1.08; $CHCl_3$), Ref. [13] oil; $\alpha_D = +25.06^o$ (c = 3.437; $CHCl_3$ at 24.8°C); MS: 340(M^+), 228, 211, 120, 91, 65, 41. IR (CCl_4): 3070, 3026, 2958, 2932, 2873, 2861, 1729, 1706, 1602, 1562, 1494, 1456, 1399, 1379, 1353, 1312, 1289, 1261, 1233, 1113, 1079, 1039, 1023 [cm^{-1}].

By the same method (S)-(+) 1-methyheptyl 4-benzyloxy-2-chlorobenzoate was obtained; oil α_D^{20} = +29° (c = 1.02; $CHCl_3$); MS: 376, 374 (M^+), 262, 245, 154, 112, 91.

(S)-(+)-1-Methylheptyl 4-hydroxybenzoate (IV): (S)-(+)-1-Methylheptyl 4-benzyloxybenzoate (16.7 g; 0.05 mole) was dissolved in tetrahydrofurane (100 ml) and debenzylated with hydrogen under atmospheric pressure in the presence of 10% palladium on charcoal (0.5 g). Temperature increased spontaneously to 35°C. After absorption of the theoretical volume of hydrogen (1.12 l) temperature decreased and reaction system was washed with nitrogen. Catalyst was filtered off and solvent was evaporated carefully.

The obtained oil was crystallized from hexane (75 ml) at –20°C. Yield 11.8 g (94%), purity 99.8% (GC); m.p. 44–46°C; $\alpha_D^{20} = +40.7°$ (c = 1.18; $CHCl_3$), Ref [13] colourless oil, $\alpha_D = +27.42°$ (c = 1.658); MS: 250(M^+), 139, 138, 121, 93, 70, 65, 41; IR (CCl_4): 3602, 3372, 3078, 2959, 2933, 2861, 1712, 1683, 1610, 1593, 1550, 1515, 1467, 1458, 1446, 1378, 1357, 1311, 1280, 1122, 1006 [cm^{-1}].

By the same method (S)-(+) 1-methyheptyl 4-hydroxy-2-chlorobenzoate was obtained, m.p. = 73–74°C; $\alpha_D^{20} = +25°$ (c = 1.04; $CHCl_3$).

3-Benzyloxypropan-1-ol (VII): Sodium (23 g; 1.0 mole) was dissolved in freshly distilled 1,3-propanediol (500 ml) by addition of small pieces of metal. (Caution! This reaction is very exothermic). When temperature extends 130°C sodium dissolves with flame. Under 90°C reaction is very slow. Then benzyl chloride (120.2 g; 0.95 mole) was added dropwise at 90–95°C and hexane (20 ml) was added. Mixture was stirred at 90–95°C for 6 h and then poured onto cold water (1 l) and extracted with benzene (3×200 ml). Combined extracts were washed with water (3×100 ml) brine (100 ml) and dried over anhydrous magnesium sulphate. Drying agent was filtered off and solvent was evaporated. Crude product was distilled through Vigreux column (20 cm length) under vacuum. Yield 105.7 g (67%), purity 98.7% (GC); b. p. 90–93°C/0.27 hPa (uncorrected); MS: 166(M^+), 147, 107, 91, 79, 65; IR (CCl_4): 3640, 3550, 3090, 3068, 3033, 2945, 2928, 2861, 2797, 1947, 1870, 1807, 1605, 1587, 1496, 1480, 1454, 1423, 1414, 1364, 1347, 1311, 1269, 1204, 1057, 1027 [cm^{-1}].

By the same method were obtained 4-benzyloxybutan-1-ol; (b. p. 105°C/0.27 hPa) and 5-benzyloxy-pentan-1-ol; (b. p. 120°C/0.40 hPa).

3-Benzyloxypropyl benzenesulfonate (VIII): To the solution of benzenesulfonyl chloride (17.7 g; 0.1 mole) in dichloromethane (100 ml) pyridine (16.0 ml; 0.2 mole) was added at room temperature. After 0.5 h the mixture was cooled down to 0°C and 3-benzyloxypropan-1-ol was dropping at 0–5°C and the mixture was put into the fridge for a night. Next morning it was poured onto ice (~100 g) with concentrated hydrochloric acid (20 ml) and CH_2Cl_2 layer was separated. Water layer was extracted with dichloromethane (50 ml) and combined extracts were washed with 5% hydrochloric acid (100 ml), water (2×50 ml), brine (50 ml) and dried over anhydrous magnesium sulphate. Drying agent was filtered off, washed with dichloromethane and combined filtrates were evaporated. Yield 30 g, 98% (oil, decomposed through distillation, during storage and on gas chromatography column). It was used without further purification for a next steep. By the same method 4-benzyloxybutyl and 5-benzyloxypentyl benzenesulphonates were obtained.

4-(3-Benzyloxyprop-1-oxy)biphenyl-4′-carboxylic acid (IX): The mixture consisting of 4-hydroxy-4′-(ethoxycarbonyl)biphenyl (24.4 g; 0.1 mole), anhydrous potassium carbonate (41.3 g; 0.3 mole), 3-benzyloxypropyl benzenesulphonate (30.6 g; 0.1 mole) and acetone (0.3 l) was refluxed with stirring until a yellow colour disappeared (8 days). Then it was poured onto a water (1 l) and extracted with chloroform (2×200 ml). Combined extracts were washed several times with water, dried over anhydrous magnesium sulphate and evaporated. Crude ester was dissolved in ethylene glycol (0.7 l), potassium hydroxide (28.0 g; 0.5 mole) was added and the mixture was refluxed with stirring for 4 h. The hot solution was poured onto cold water acidified with hydrochloric acid (80 ml) and the mixture was stirred at room temperature for 6 h. The separated crystals were filtered off, washed with plenty of water, ethanol (100 ml) and crystallized from ethanol-tetrahydrofurane (1.5 l, 3:1 v/v) and then from toluene (0.5 l). Yield 30.6 g (84.6 %); Cr 180 SmX 217 N 225 Iso. By the same method 4-(4-benzyloxybut-1-oxy)biphenyl-4′-carboxylic acid; (Cr 158 SmX 214 N 230 Iso) and 4-(5-benzyloxypentyl-1-oxy)bi-phenyl-4′-carboxylic acid were obtained; Cr 171 SmX 218 Iso.

(S)-(+)-4-(1-Methylheptyloxycarbonylphenyl) 4-(3-benzyloxyprop-1-oxy)biphenyl-4′-carboxylate (XI): Compound was obtained by the same way as (S)-(+)-1-methylheptyl 4-benzyloxybenzoate (IV) starting from 4-(3-benzyloxyprop-1-oxy)biphenyl-4'-carboxylic acid (IX) and (S)-(+)-1-(1-methylheptyl) 4-hydroxybenzoate (V). Crystallization from ethanol-acetone. Purity was checked by TLC. Yield 75.6%; Cr 57 SmC^* 107 Iso. IR (CCl_4): 2958, 2933, 2861, 1743, 1718, 1606, 1525, 1505, 1472, 1458, 1413, 1261, 1205, 1183, 1162, 1112, 1065, 1015, 1003 [cm^{-1}].

By the same method (S)-(+)-4-(1-methylheptyloxycarbonylphenyl) 4-(4-benzyloxybut-1-oxy)biphenyl-4′-carboxylate; (Cr 86 (SmX 76) SmA 102 Iso) and (S)-(+)-4-(1-methylheptyloxycarbonylphenyl) 4-(5-benzyloxypentyl-1-oxy)biphenyl-4′-carboxylate; (Cr 63 SmA 131.8 Iso) were obtained.

(S)-(+)-4-(1-Methylheptyloxycarbonylphenyl) 4-(3-hydroxyprop-1-oxy)biphenyl-4′-carboxylate (XII): Compound was obtained by the same way as (S)-(+)-1-(1-methylheptyl) 4-hydroxybenzoate (V). Crystallization from hexane-chloroform (4:1 v/v). Yield 65%; Cr 140 SmA 167 Iso; $\alpha_D^{20} = +25°$ (c = 1.38; $CHCl_3$); IR (CCl_4): 3640, 2957, 2932, 2861, 1743, 1718, 1606, 1526, 1506, 1472, 1261, 1204, 1183, 1162, 1113, 1065, 1016, 1003 [cm^{-1}].

By the same method (S)-(+)-4-(1-methylheptyloxycarbonylphenyl) 4-(4-hydroxybut-1-oxy)biphenyl-4′-carboxylate (Cr 135 (SmX_1 104) SmX_2 170 Iso) and (S)-(+)-4-(1-methylheptyloxy-carbonylphenyl) 4-(5-hydroxypentyl-1-oxy)biphenyl-4′-carboxylate; (Cr 101 SmA 153,4 Iso) were obtained. The final compounds (XIII) of series nHm-A, nHm-B, nFHm-A, 1FnHm-A presented in Table 1 were obtained by acylation of appropriate alcohols (XIII) with acyl chlorides (method A) or from alcohols (XIII) and acids *via* Mitsunobu reaction method (B).

(S)-(+)-4-(1-Methylheptyloxycarbonylphenyl) 4-(3-heptafluorobutanoyloxyprop-1-oxy)-biphenyl-4′-carboxylate (XIII, 3FH3-A). Method A: To a stirred mixture consisted of compound 12 (5.0 g; 9.9 mmol), pyridine (5.0 ml; 62.5 mmol), 4-N,N-dimethylaminopyridine (catalytic amount) and toluene (50 ml) heptafluorobutyryl chloride was added (1.8 ml; 12 mmol). Temperature raised spontaneously to 40°C and pyridine hydrochloride precipitated. After finishing of the exothermic reaction stage the mixture was stirred for 12 h at 50°C and after cooling was poured onto 100 ml of 5% hydrochloric acid. The toluene layer was separated and washed 3 times with 5% hydrochloric acid, then with water (2×50 ml) and brine (1×25 ml), dried over anhydrous magnesium sulphate and filtrated. Toluene was removed by evaporation. The solid was dissolved in 250 ml of hot (~80°C) heptane and solution was passed through the thermostated chromatographic column (80°C) filled with silica gel (l = 5 cm, ϕ = 2 cm). The column was washed with hot heptane. The combined filtrates were evaporated to dryness. The obtained solid was crystallized three times from ethanol (170 cm^3). Its purity was tested by TLC on silica-gel plates, developed with $CHCl_3$ and mixture $CHCl_3$-hexane (9:1). In these conditions only one spot was observed. Aluminum oxide plates caused fast decomposition. Yield 5.6 g (79.2 %). IR (KBr): 2962, 2937, 2865, 1785, 1728, 1702, 1603, 1561, 1529, 1502, 1472, 1413, 1356, 1278, 1231, 1216, 1189, 1160, 1115, 1075, 1015, 1002, 974, 952, 886, 863, 837, 807, 769, 732, 722, 690, 651, 628, 552, 519 [cm^{-1}].

By this method the following compounds: 1, 3, 5, 7, 8, 11, 13, 16, 17, 18, 19, 21 were obtained. In the case of compounds 2 and 4 instead of acid chlorides adequate acid anhydrides were used.

(S)-(+)-4-(1-Methylheptyloxycarbonyl)phenyl 4-[3-(4,4,4-trifluorobutanoyloxy)prop-1-oxy]biphenyl-4-carboxylate (XIII, 1F2H3-A). Method B: To a mixture of S-(+)-4-(1-methylheptyloxycarbonyl)phenyl 4-(3-hydroxyprop-1-oxy)biphenyl-4'-carboxylate (XI) (2.0 g; 4.0 mmol), 4,4,4-tri-

fluorobutanoic acid (0.3 g, 4.1 mmol), triphenylphosphine (1.2 g; 4.6 mmol) in anhydrous tetrahydrofurane (30 ml) diethyl azodicarboxylate (0.72 ml; 4.6 mmol) was added. The mixture heated itself spontaneously to 25°C and a yellow color diminished. It was stirred for 24 h and then tetrahydrofurane was distilled off. The solid was crystallized from ethanol and purificated on chromatography column (silica-gel, chloroform) and then crystallized twice from ethanol (150 cm^3). Purity was checked by TLC (silica-gel and aluminum oxide; $CHCl_3$ and hexan-$CHCl_3$ (9:1)); $[\alpha]_D^{20} = +20°$ (c = 0.98; $CHCl_3$); yield 1.8 g (69%). IR (KBr): 2957, 2931, 2860, 1734, 1710, 1604, 1529, 1507, 1499, 1470, 1444, 1426, 1415, 1402, 1381, 1340, 1310, 1286, 1232, 1196, 1167, 1136, 1119, 1072, 1015, 1000, 985, 956, 919, 889, 961, 827, 813, 795, 766, 730, 718, 691, 634, 545, 493 [cm^{-1}]. By the same method the following compounds: 10, 12, 14, 15 and 20 were obtained.

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