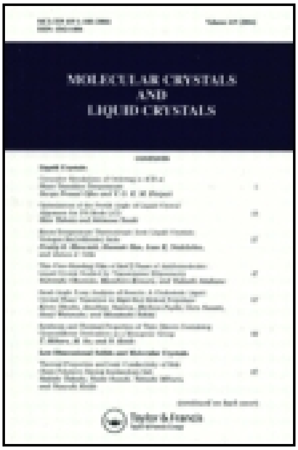

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Antiferroelectric Compounds with trifluoromethyl group in ω-Position of Terminal Chain

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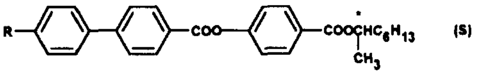
Chiral (S) 4-(1-methylheptyloxycarbonyl)phenyl 4'-(ω-trifluoroethoxyalcoxy)biphenyl-4-carboxylates and 4'-(ω-trifluoro-butanoyloxyalcoxybiphenyl)carboxylates were prepared and their phase transitions and the temperature dependence of the smectic layer spacings, tilt angle, spontaneous polarization, threshold and switching times for the antiferroelecrtic – ferroelectric transition were measured.

Keywords: antiferroelectrics; phase transitions; smectic layer spacings; spontaneous polarization; tilt angle; switching parameters

INTRODUCTION

As we have shown recently [1] it is possible to obtain compounds having a smectic antiferroelectric phase (SmC_A^*) also when they contain terminal chain R substituted by many fluorine atoms in an analogous structure to MHPOBC, formula I



(I)

The presence of the SmC_A^* phase was observed for R= $C_nF_{2n+1}COO(CH_2)_mO$ (perfluoroalkanoyloxyalcoxy group) and n=1÷7. The big differences in phase diagrams and physical properties of the smectic phases were observed between these compounds and their non-fluorinated analogues [2]. Therefore it seems to be interesting to prepare further compounds substituted with fluorine according to better known relations between a structure of fluorinated terminal chain R and the properties of the antiferroelectric smectic phase which in result would contribute to enlargement of the assortment of compounds able to be applied in displays.

STUDIES OF PHYSICAL AND PHYSICOCHEMICAL PROPERTIES

Phase transitions

The detailed description of the preparative procedure for compounds with R in the form of $CF_3CH_2O(CH_2)_mO$ and $CF_3CH_2CH_2COO(CH_2)_mO$ (series 1 and 2) are given in a Ph.D. thesis [3] and in the paper [4]. Phase transition temperatures and enthalpies for series 1 and 2 are listed in Table I and are compared with the ones having the terminal chain in the form of $CH_3CH_2O(CH_2)_2O$ or $CH_3CH_2CH_2COO(CH_2)_mO$ or $CF_3CF_2CF_2COO(CH_2)_mO$ [5]. The presence of CF_3 group in the terminal position of the chain strongly favors appearance of the tilted phases, especially the SmC_A^* one. This phase was observed in series 1 even for the members with a very short terminal chain R while for their hydrogen analogues (see 1a') only the smectic A phase above the melting point was seen.

TABLE I Temperatures (°C) and enthalpies (kcal/mol, second line) of phase transitions for compounds of series 1, 2, 3 and 4 from DSC; experimental procedure the same as in [5].

No	R	Cr		SmI_A^*		SmC_A^*		SmC^*		SmA		Iso
1a	CF_3-$CH_2O(CH_2)_2O$-	•	107.4	-		•	127.0	-		•	151.2	•
			6.25				0.06				1.30	
1a'	CH_3-$CH_2O(CH_2)_2O$-	•	102.3	•	(90.5)[a]	-		-		•	148.1	•
			6.20								1.90	
1b	CF_3-$CH_2O(CH_2)_3O$-	•	106.6	-		•	123.5	-		•	134.0	•
			8.3				0.10				1.20	
1c	CF_3-$CH_2O(CH_2)_4O$-	•	121.3	-		•	127.0	•	133.0	•	145.6	•
			7.90				0.02		0.10		1.30	
1d	CF_3-$CH_2O(CH_2)_5O$-	•	75.2	-		•	126.7	•	127.3	•	137.3	•
			6.50				0.10		0.00		1.10	
2a	$CF_3CH_2CH_2COO(CH_2)_3O$-	•	99.0	-		•	111.3	•	122.2	•	126.8	•
			6.6				0.02		0.12		1.28	
2b	$CF_3CH_2CH_2COO(CH_2)_4O$-	•	87.4	-		•	112.0	•	114.8	•	116.9	•
			9.5				0.03		0.16		0.81	
3a	$CH_3CH_2CH_2COO(CH_2)_3O$-	•	67.0	•	(43.0)	•	92.8	-		•	116.2	•
			5.04		0.3		0.09				1.3	
3b	$CH_3CH_2CH_2COO(CH_2)_4O$-	•	69.9	-		•	91.5	•	100.6	•	110.6	•
			8.5				0.02		0.08		1.00	
4a	$CF_3CF_2CF_2COO(CH_2)_3O$-	•	83.5	•	(54)	•	121.0	•	123.6	•	128.8	•
			4.42				0.02		0.28		0.73	
4b	$CF_3CF_2CF_2COO(CH_2)_4O$-	•	69.8	-		•	120.7	•	125.6	-		•
			3.01				0.00		1.08			

a - in the recent work [5] we termed this monotropic phase as B_{hex} but our further miscibility study and the observation of the change black monotropic texture to transparent one during the transition gave evidence that it is a tilted I_A phase.

An increase of the length of spacer in the all listed series decreases the melting points, clearing points and the range of SmA phase but do not depress tilted phases SmC_A and SmC.

Smectic layer spacings

The temperature dependence of smectic layer spacings (d) for compounds series 1-4 are given respectively in Figure 1a, b, c, d. For series 1 the compounds having the even number of atoms in the terminal chain R (1a and 1c, respectively 6 and 8 atoms) show thicker smectic layer spacings in the smectic A phase as well as in the smectic C_A^* phase than the following members having the odd number of atoms in this chain: (1b and 1d, respectively 7 and 9 atoms), Figure 1a. For series 2, 3 and 4 the compounds 2a, 3a, 4a having the odd number of atoms in R (nine) exhibit the thicker smectic layer spacings than the following ones: (2b, 3b, 4b; ten atoms), Figure 1b, c and d.

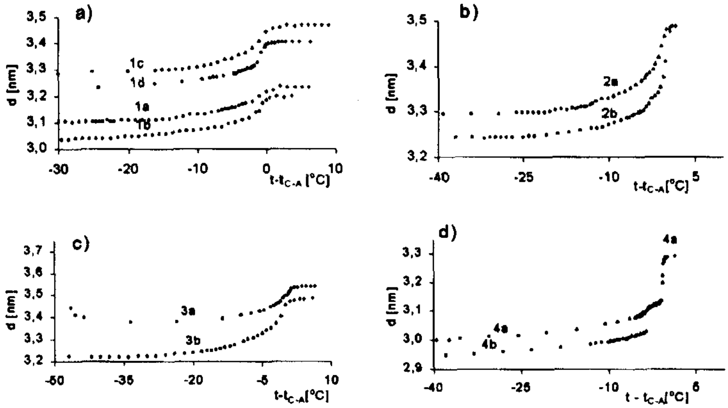


FIGURE 1 The smectic layer spacing versus temperature for the compounds of series: 1 (a), 2 (b), 3 (c) and 4 (d), for 4b t_{iso} was taken instead of $t_{C\text{-}A}$; X-ray DRON-UH2 diffractometer and the semifree film of the liquid crystal (the liquid crystal was placed on a single glass support) were used.

The increase of the chain R results in decreasing of the ratio d/d_A, (d_A-layer spacing for SmA phase), Figure 2; these molecules are more tilted in the smectic layers. The ratio d/d_A changes with temperature in the most rapid way for the compound 1c in which the chain R contains four methylene group as the spacer (m=4). The same was found for series 2, 3, 4 where the ratio d/d_A were also smaller for compounds with m=4 for the same $t\text{-}t_{C\text{-}A}$.

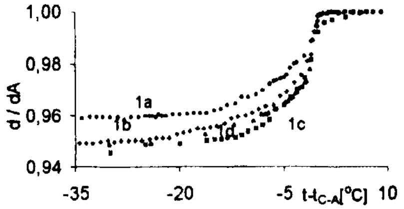


FIGURE 2 Comparison of the change of the ratio d/d_A upon temperature in series 1.

The data listed in Table II lead to the conclusion - the exchange of the methyl end group (CH_3) for the trifluoromethyl group (CF_3) in the chain $CH_3CH_2O(CH_2)_mO$ or $CH_3CH_2CH_2COO(CH_2)_mO$ causes the decrease of the smectic layer breadth in the SmA phase (d_A) as well as in the SmC_A phase in spite of the longer molecules. Simultaneously the ratio d_{C^*A}/d_A decreases and tilt angles θ_{opt} and θ_1, θ_2, θ_3 increase.

TABLE II Comparison of the data for the smectic layers from X-ray scattering. The tilt angles: θ_1, θ_2 and θ_3 - arccos (d_{C^*Amin}/d_A or $d_{C^*A\,min}/l$ or $d_{C^*A\,(20)}/l$) and θ_{opt} from optical measurements.

No	l^a [nm]	d_A [nm]	$d_{C^*A\,min}$ [nm]	$d_{C^*A\,min}/l$ [nm]	d_A/l	d_{C^*A}/d_A	θ_1 (max) [deg]	θ_2 [deg]	θ_3 (20)^b [deg]	θ_{opt} (20)^b [deg]
1a	3.577	3.23	3.10	0.867	0.903	0.960	29.9	16.3	29.6	23.2
1a'	3,491	3,43^c	-	-	0.982^c	-	-	-	-	-
1b	3.712	3.20	3.04	0.819	0.862	0.950	35.0	18.2	34.7	28.1
1c	3.765	3.47	3.28	0.871	0.922	0.945	29.4	19.0	29.1	29.0
1d	3.960	3.40	3.23	0.816	0.859	0.950	35.3	18.2	35.1	33.8
2a	3.811	3.44	3.25	0.853	0.903	0.945	31.5	19.1	31.5	31.3
2b	3.765	3.43	3.19	0.847	0.911	0.930	32.1	21.6	31.8	34.4
3a	3.779	3.49	3.33	0.881	0.924	0.954	28.2	17.4	28.2	24.3
3b	3.771	3.44	3.17	0.841	0.912	0.922	32.8	22.9	-	30.7
4a	3.811	3.29	3.00	0.787	0.863	0.912	38.1	24.2	37.3	39.0
4b	3.842	-	2.93	0.763	-	-	40.3	-	39.6	40.3

a - HyperChem program; b-at distance of 20°C from transition to A phase;
c - maximum value, d_A increases with temperature decrease.

The enlargement of the fluorinated part of the chain R (the change of $CF_3CH_2CH_2$- group for $CF_3CF_2CF_2$-) involves further diminishing of the layer spacings in the both above mentioned phases and an increase of the tilt. The largest values of tilts (39 deg and 40 deg) were found for compounds 4a and 4b with the chain $CF_3CF_2CF_2COO(CH_2)_m$ (m=3 and 4 respectively). The molecules with methylene spacer m=4 in the series 2, 3 and 4 and with m=5 for series 1 have the largest tilts.

Spontaneous polarization and antiferroelectric-ferroelectric transition

The spontaneous polarization and switching properties measured for temperature 20°C and 30°C below the transition to the SmA phase ($t-t_A$) are listed in Table III.

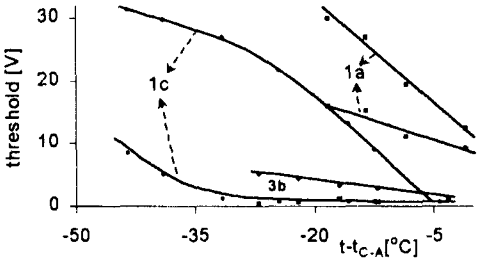


FIGURE 3 Temperature dependence of threshold voltages V_{10} and V_{90} for compounds 1a, 1c and 3b.

The polarization values change in the range of 100÷300 nC/cm^2, but they are different from the ones resulting from the relation between the value of the polarization and the structure of the alkyl tail R. For the same pairs of analogous compounds with fluorinated and nonfluorinated chains the fluorinated ones have a larger polarization (see the examples of the compounds 3a and 4a) but for the other pair (see 3b and 4b) both compounds have a large spontaneous polarization. Such situation may be understood if we take into account the fact that only molecules with hindered rotation participate in the creation of spontaneous polarization [6,7]. According to Raszewski et al. calculations concerning the molecules with chiral center $COOCH(CH_3)C_6H_{13}$ less than a dozen percentage of all ones [7] stopped their rotation and therefore small effects may influence the equilibrium between hindered and free rotated molecules. Threshold voltages and the shape of hysteresis curves have strongly individual characters, see Figure 3, but some relation with the structure of R are seen.

TABLE III Comparison of spontaneous polarization (Ps) and electrooptical data for antiferroelectric-ferroelectric transition (F) (V_{10}, V_{90}, $\tau_{0\text{-}50}$, $\tau_{50\text{-}0}$, $\tau_{-50++50}$) for compounds of series 1-4 at temperature 20 and 30°C below transition to smectic A phase.

No	V_{10} [V]	V_{90} [V]	Ps [C/cm^2]	$\tau_{(0\text{-}50)}$ [μs]	$\tau_{-(50++50)}$ [μs]	$\tau_{(50\text{-}0)}$ [μs]
1a	29.0	15.7	100	24	30	35
	-	-	100	28	32	35
1b	16.6	6.1	170	25	28	56
	-	-	-	30	34	60
1c	17.6	9.9		-	-	-
	25.2	1.3	-	-	-	-
1d	21.6	12.1	170	34	24	57
	23.9	14.4	190	41	27	63
2a	11.5	1.2	150	-	-	-
	15.3	1.2	175	11	30	68
2b	11.3	3.4	180	37	38	200
	14.6	4.8	-	51	45	180
3a	20.2	7.7	130	31	26	154
	24.3	4.3	165	41	27	133
3b	4.1	1.0	210	14	27	126
	5.6	0.3	280	19	35	105
4a	10.0	1.3	300	20	28	42
	14.7	1.5	340	22	33.5	41
4b	-	-	170	-	-	-
	7.9	1.9	200	12	41	71

V_{10} - transmitance reaches the value of 10%; V_{90} -transmitance falls to 90%. All measurements were done in the glass cells 13x15 mm with ITO electrodes 5x5 mm (resistivity 100-200 Ohm). The cells gap was 1.7 μm. The SmC_A^* had planar alignment mode by parallel rubbed nylon-6 (20 nm thick). Spontaneous polarization was measured by the triangle wave form method [9] at 100 Hz.

The all fluorinated compounds of series 1 have high values of V_{10} and they are much higher than for the fluorinated esters 2 and 4. In series 1 the values of V_{90} are very different, the members 1a and 1d show the large value of V_{90} but 1b, 1c show the small value of V_{90}.

Nonfluorinated esters 3a have also a large threshold V_{10} and a broad hysteresis curve, but members with m=4 have the smallest threshold voltages V_{10} and V_{90}. It seems that the correlation between threshold voltages and the tail structure exists and the compounds with methylene spacer m=4 have smaller both threshold voltages V_{10} and V_{90}. In majority of cases the increase of temperature reduces the voltages V_{10} and V_{90} and differences V_{10}-V_{90} near transition to C^* phase falls to zero and some cases of thresholdless transition AF-F is observed [8].

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References

[1] W. Drzewiński, R. Dąbrowski, K. Czupryński, J. Przedmojski, M. Neubert, *Ferroelectrics*, **212,** 281 (1998).
[2] A. Fąfara, B. Gestblom, S. Wróbel, R. Dąbrowski, D. Kilian, W. Haase, *Ferroelectrics*, **212,** 79 (1998).
[3] W. Drzewiński, „Synteza i analiza właściwości ciekłokrystalicznych nowych związków z fazą antyferroelektryczną" Ph.D.Thesis, Warsaw (1999), in preparation.
[4] W. Drzewiński, K. Czupryński, R. Dąbrowski, M. Neubert, *Biulletine of Military University of Technology,* **47** (7–8), 53 (1998).
[5] W. Drzewiński, K. Czupryński, R. Dąbrowski, M. Neubert, *Mol. Cryst. Liq. Cryst.*, in press (1999).
[6] Z. Raszewski, J. Rutkowska, J. Kędzierski, P. Perkowski, W. Piecek, J. Zieliński, J. Żmija and R. Dąbrowski, *Mol. Cryst. Liq. Cryst.*, **263,** 271 (1995).
[7] Z. Raszewski, J. Rutkowska, J. Kędzierski, P. Perkowski, W. Piecek, J. Zieliński, J. Żmija, R. Dąbrowski, *Mol. Cryst. Liq. Cryst.*, **302,** 85 (1997).
[8] V.A. Konovalov, A.A. Muravski, S. Yakovenko, W. Drzewiński, K. Czupryński, R. Dąbrowski, *Ferroelectrics*, in press (1999).
[9] K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, E. Kuze, *Jap. J. Appl. Phys.*, **22,** L661 (1983).