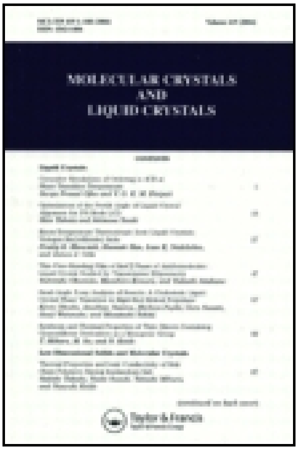

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New Antiferroelectric Compounds Containing Partially Fluorinated Terminal Chains. Synthesis and Mesomorphic Properties

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New Antiferroelectric Compounds Containing Partially Fluorinated Terminal Chains. Synthesis and Mesomorphic Properties

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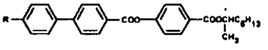
Methods for preparing optically active hydroxyesters: 1-hydroxy-4-(1-methylheptyloxycarbonyl)benzene and 4-hydroxy-4′-(1-methylheptyloxy-carbonyl)biphenyl, 4-(1-methylheptyloxycarbonyl)phenyl 4′-hydroxybiphenyl-4-carboxylate and 4′-(l-methylheptyloxy carbonyl)biphenyl-4-yl 4-hydroxybenzoate have been elaborated. These compounds were used as intermediates for preparing liquid crystalline homologous series of di- and triesters exhibiting tilted smectic phases C_A^* and C^*. The phase transitions have been measured by DSC and thermomicroscopic methods and the smectic phases have been identified by microscopic textures and miscibility studies.

Keywords: synthesis of liquid crystals; optically active esters; ferro- and antiferroelectrics; phase transitions

INTRODUCTION

Liquid crystals with antiferroelectric (AF) properties are very promising future LC materials. They make it possible to build both small and large fast switching flat panels with high density information contents, which may be driven passively and actively[1,2]. Compounds with a trifluoromethyl group in the neighborhood of a chiral center are the most interesting, because most of them have a broad range antiferroelectric phase (SmC_A^*) and a high value of spontaneous polarization[3-6]. It is suggested increasing the polarity at the chiral center of a molecule promotes a larger value for the spontaneous polarization in the ferroelectric state created from an antiferroelectric one by a change of the electric field[3]. We have decided to prepare compounds with higher polarity by introducing a fluorinated moiety into the terminal chain opposite to the chiral center to gain the knowledge on how such a modification influences the ability to exhibit the SmC_A^* phase. Esters containing a fully fluorinated or a partially fluorinated chain in the acid or phenol moiety are known[4,7,8], but the reported compounds did not show antiferroelectric properties. In our previous short papers[9,10] we have showed a structure with the fluorinated terminal chain in which the antiferroelectric phase exists in a broad temperature range. This result has promoted us to perform more systematic studies on the reported homologous series as well as on other structurally similar groups. In this paper, we describe the synthesis method for compounds having the general formula I and II: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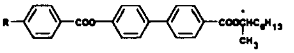

II

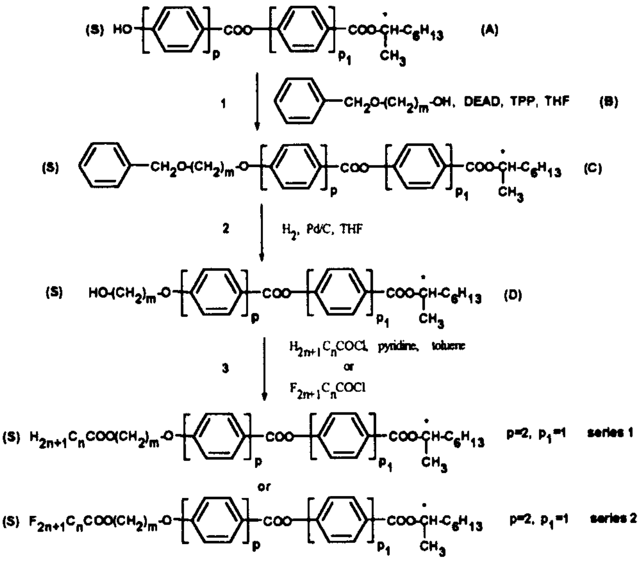
R: $H_{2n+1}C_nCOO(CH_2)_mO$- – compounds of series 1,
$F_{2n+1}C_nCOO(CH_2)_mO$- – compounds of series 2,
$H_{2n+1}C_nO(CH_2)_mO$- – compounds of series 3,
F_3C-CH_2-$O(CH_2)_mO$- – compounds of series 4,
$F_{13}C_6$-CH_2-CH_2-O- – compound 5,

R: $F_{13}C_6$-CH_2-CH_2-O- – compounds of series 6,
$H_{2n+1}C_nO(CH_2)_mO$- – compounds of series 7,
F_3C-CH_2-$O(CH_2)_mO$- – compounds of series 8,

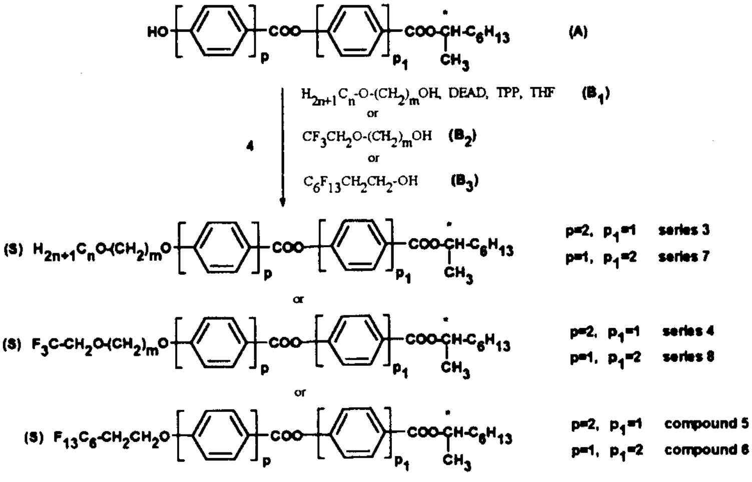
Some compounds of series 3 and 7 are known from the references[11,12] but we found that their phase sequence should be revised.

SYNTHESIS OF THE FINAL ESTERS

The target compounds of series 1 and 2, 4-(1-methylheptyloxycarbonyl)-phenyl 4'-(alkanoyloxyalkoxy)- and 4'-(perfluoroalkanoyloxy)biphenyl-4-carboxylates were prepared according to the route outlined in scheme 1:



SCHEME 1 Route of synthesis of compound 1 and 2.

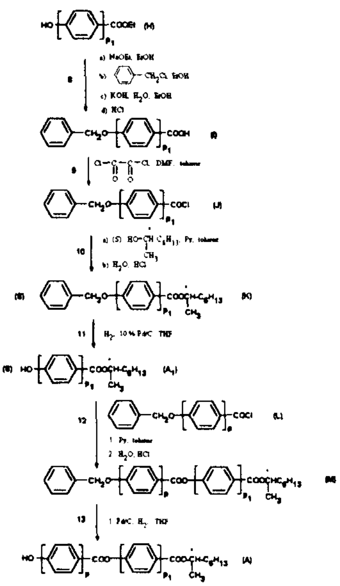


SCHEME 2 Synthesis route of the compounds of the series 3 and up to 8.

The hydroxyester A (scheme 1) was alkylated with ω-benzyloxyalcohol in the presence of triphenylphosphine (TPP) and diethylazodicarboxylate (DEAD) (Mitsunobu reaction[13]). The resulting compound C with two ether bonds in the terminal chain - the first one at the benzyl moiety and the second one at the phenyl moiety - was debenzylated using gaseous hydrogen in the presence of palladium on carbon. The resulting alcohol D was converted to the final ester 1 or 2 by the action of alkanoylcarbonyl or perfluoroalkanoylcarbonyl chloride in the presence of pyridine in toluene solution. The compounds of series 3, 4, 5, 6, 7 and 8 were prepared starting from A or a similar reactant in one-stage Mitsunobu reaction shown in scheme 2.

Synthesis of the Semiproducts

The route for the preparation of the optically active monohydroxyester A_1 and the hydroxybiester A is presented in scheme 3.



SCHEME 3 The route of synthesis of optically active esters A and A_1.

For the preparation of the hydroxyesters A_1 and hydroxydiester A, the benzyl group was used to protect the free hydroxy group in the acid moiety, forcing the esterification reaction to go in the desired direction. After the formation of the ester bond, the benzyl group was removed by hydrogenation in the presence of Pd/C catalyst. The hydroxy group was then ready for esterification or etherification. In the other works, for example[14], the alkylchloroformate was used for protection of the hydroxy group. The resulting carbonate ester was then converted to the phenol by stirring at room temperature in an ethanolic ammonia solution. We believe, that the benzyloxy group serves as a better protective group than the carbonate one. In our method, the benzyl ethers K and M separate well and their purification is easy. The hydrogenation products A_1 or A showed high purity and the yields were excellent. Commercially available S(+)-octanol-2 (Fluka) was used as the optically active starting material. It was esterified with acid chloride in the presence of pyridine in toluene. This method did not allow for racemisation and there was no change in the absolute configuration of the chiral center, so that the final esters had the same configuration as the starting alcohol. MHPOBC which was prepared using the some conditions, as described above, had the C subphases at the same temperatures as described in the literature[15]. It is known, that the subphases C_γ and C_α are observed only in the materials of high optical purity[3]. This confirms that the method of synthesis used by us gives compounds with good optical purity.

MESOMORPHIC PROPERTIES

The transition temperatures of the compounds from series 1-7 measured using a polarizing microscope with a hot stage and a differential scanning calorimeter, on cooling, are listed in Table I.

TABLE I Temperatures and enthalpies of phase transitions

In the first line temperatures (°C) are from thermomicroscopic measurement, in the second line from DSC, and in the third line the values of enthalpies (kcal/mol) are given

	n	m	Cr$_1$		Cr		SmI$_A$		SmC$_A$		SmC		SmA		I
1a	1	3	•		•	60	•	(56)	-		-		•	130	•
				55.8		58.7		(56.8)						131.0	
				1.42		2.23		0.15						1.30	
1b	2	3	•			77	•	(46)	•	88.0	-		•	123.2	•
				30.0		77.2		(47.2)						123.0	
				1.86		5.50		0.15						1.30	
1c	3	3	-		•	67.0	•	(41.6)	•	92.3	-		•	116.9	•
						67.0		(43.0)		92.8				116.2	
						5.04		0.3		0.09				1.3	
1d	4	3	•		•	60	•	(30.0)	•	91.9	-		•	111.5	•
				42.5		59.0		(31.9)		91.6				110.9	
				4.40		3.90		0.12		0.07				1.28	
1e	5	3	-		•	72	•	(24.5)	•	92.1	-		•	109.1	•
						72.4		(26.3)		90.8				108.7	
						8.50		0.24		0.16				1.35	
1f	6	3	-		•	50.0	•	(16)	•	89.7	•	91.7	•	105.7	•
						50.4		(22.0)		90.4		92.8		105.8	
						7.87		0.19		0.02		0.04		1.21	
1g	7	3	•		•	49	•	(22)	•	88.7	•	91.5	•	105.3	•
				37.2		49.3		(25.0)				91.4		105.5	
				2.85		4.6		0.10				0.04		1.4	
2a	1	3	-		•	82.0	-		•	120.4	•	124.5	•	130	•
						82.0						124.6		129.2	
						4.4						0.09		0.90	
2b	2	3	-		•	104	•	(45)	•	119.9	•	122.5	•	125.3	•
						102.9						121.5		124.7	
						5.40						0.12		0.69	
2c	3	3	-		•	83.6	•	(54)	•	119.7	•	123.5	•	128.8	•
						83.5				121.0		123.6		128.8	
						4.42				0.02		0.28		0.73	
2d	7	3	•		•	69	-		•	100.0	•	124.5	•	153.8	•
				56.6		68.8						123.7		153.2	
				0.15		4.56						0.12		1.14	
2e	3	4			•	70.0	-		•	120.7	•	126.1	-		•
						69.8						125.6			
						3.01						1.08			
3a	2	2			•	102	•	(91)^a	-		-		•	148.5	•
						102.3		(90.5)						148.1	
						6.20		1.40						1.90	
3b	4	3			•	74							•	124.5	•
						73.3								125.0	
						3.97								1.30	
4a		2			•	108.9			•	128.7			•	153.3	•
						107.4				127.0				151.2	
						6.25				0.06				1.3	
4b		3			•	105.4			•	123.7	-		•	134.0	•
						106.6				123.5				134.0	
						8.30				0.10				1.20	
5a			•		•	98.7					•	150.4	•	184.4	•
				80.7		98.9						149.0		184.0	
				2.50		4.18						0.20		1.10	
6					•	101.7	-		-		•	156.3	•	186.5	•
						94.3						155.0		184.0	
						4.48						0.22		0.95	
7a	4	3			•	91.8	-		-		-		•	(90.1)	•
						90.5								(88.6)	
						9.54								1.30	

a - S_{Bhex}.

Liquid crystalline smectic phases were identified on the bases of their textures, miscibility with standard compounds and X-ray studies. The X-ray results are discussed in another paper[16]. The phase diagrams of mixtures containing compounds 1-7 and standard compounds and mixtures of compounds 1-7 are presented in our other paper[17].

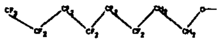
DISCUSSION OF RESULTS

In the homologues series containing compounds 1-7 the antiferroelectric SmC_A^* phase has been observed for compounds 1, 2, 3 and 4 respectively. The thermal stability of the SmC_A^* phase, and the phase sequence, which is correlated with it, in a deciding way depends on the structure of the terminal chain. Not only the total length is important, but also a mutual relationship between different parts of the chain (the value of n and m index) and the presence of additional polar groups. We can see from the data in Table I that small changes in the structure of a terminal chain opposite to the chiral center involve drastic changes in the phase sequence. The replacement of the octyloxy chain in MHPOBC with the 1H,1H,2H,2H-perfluorooctyloxy chain, of nearly the same length, (compound 5) results in the disappearance of the SmI_A^* and SmC_A^* phases and the simultaneous great increase in the thermal stability of the SmC^* phase and especially the SmA phase. Such effects, caused by partial or full fluorination of an alkyl chain is typical and it was already observed by Janulis in the case of esters when the fluorinated chain was attached to a phenol or acid moiety[8]. The same behavior was observed by Liu in the case of partially fluorinated phenyl pyrimidines[18]. The separation of the perfluoroalkyl part of the chain from the alkoxy part by the carboxylic bridge leads to the presence of the antiferroelectric SmC_A^* phase - the compounds of series 2. The mesomorphic properties of the obtained compounds having the same number of atoms in the main terminal chains as in MHPOBC are listed below; only the fragments of molecules that are different are shown.

MHPOBC

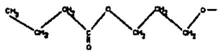
$Cr\ 84\ (I_A^*\ 65)\ C_A^*\ 118{,}4\ C_\gamma^*\ 119{,}2\ C_\beta^*\ 120{,}9\ C_\alpha^*\ 122\ A\ 148\ I$

5



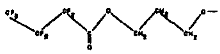
$Cr\ 98{,}9\ C^*\ 149\ A\ 184\ I$

1c



$Cr\ 67{,}0\ (I_A^*\ 43{,}0)\ C_A^*\ 92{,}8\ A\ 116{,}2\ I$

2c



$Cr\ 83{,}5\ (I_A^*\ 54{,}0)\ C_A^*\ 121\ C^*\ 123.6\ A\ 128{,}8\ I$

The above comparison shows that compound 2c (containing perfluorobutanoyloxyprop-1-oxy chain) exhibits the same main phases as MHPOBC but the subphases of the smectic C^* phase are not seen. The lengthening of fluorinated part of the terminal chain in the homologous series 2 does not change the thermal stability of the smectic C^* phase, but slightly decrease the stability of the smectic C_A^* phase at the expense of the smectic A stability. Such a relationship was found in 2. This is no longer true for compounds in the series for which index m has a value of 4. Compounds with m=4 (see 2e, Table I) do not exhibit the A phase. Compound 2e shows the phase sequence Cr-C_A^*-C^*-I. Compounds from homologous series 2 show a greater ability to form the smectic C^*_A phase than compounds from series 1 do. It is observed for members with a shorter chain (even for the smallest value of m=1 and when the total number of carbon atoms is only 7). In the case of series 1 (without the fluorinated part of the terminal chain - alkanoyloxyalkoxy chain) the smectic C_A^* phase is observed when m=2. Furthermore, compounds 1 show the presence of smectic C phase only for chains characterized by n≥6. Such results for the series 1 and 2 indicate that the tilted smectic C^* and C_A^* phases become more stable with the fluorination extent irrespective of the terminal chain length. The comparison of the compounds of series 2 and 4 shows that replacement of trifluoroacetyloxy group (compound 2a) by the 2,2,2-trifluoroethoxy group (compound 4b) slightly increases the stability of the smectic C_A^* phase at the expense of the smectic C^* phase; the stability of the smectic A phase is also a little higher. The replacement of the 2,2,2-trifluoroethoxy group by the etoxy one involves the disappearance of the smectic C_A^* in compound 3a. The clearing temperatures and the thermodynamic stabilities of the smectic A phase in compounds 3a and 4a are similar. Their structural features, which are responsible for dimerization, a factor necessary for the creation of the smectic C_A^* phase, must be quite different and therefore the smectic C_A^* phase is not observed in compound 3a. In compound 3a only the hexatic smectic B phase exists below the smectic A phase. Compound 3a was already reported in Ref.[11]. The phase sequence Cr 100.5 (E 89.8) A 147.0 I and the monotropic character of the smectic E phase was given. The results presented above give direct evidence, that it is possible to produce compounds having a broad temperature range for the antiferroelectric phase when their molecules have their terminal chain fluorinated. Our preliminary studies of the physical properties of the such fluorinated compounds showed that they have values of spontaneous polarization and cone tilt angles higher than their hydrogen analogues[19].

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