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LATERALLY BRANCHED MESOGENS INCORPORATING A RIGID PERFLUOROALKYL CHAIN

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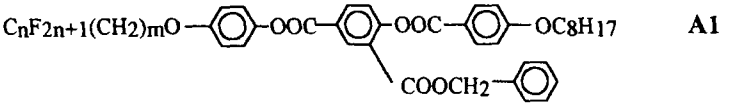
Abstract We synthesized laterally aryl substituted mesogens derived from isophthalic acid (type **A**) and resorcylic acid (type **B**) containing a fluorinated alkyl-alkoxy chain in a terminal position. An increase of the clearing points and a stabilization of the smectic phases compared to the nonfluorinated references appear in all cases. Hereby, the position is not important for the height of the transition temperatures. There is a dependence on the number of methylene units between the oxygen and the fluoro-carbon groups in the type **A** derivatives.

INTRODUCTION

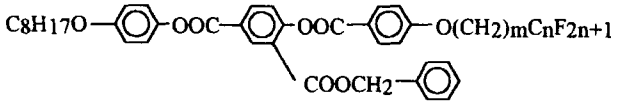
The field of the laterally substituted mesogens is very large. Often they are three-ring molecules with the branch at the first or second aromatic core. Hereby, the size of the lateral substituent can be varied from single atoms and small groups to long alkyl chains and aromatic units [1,2]. The class of the laterally aryl substituted compounds is well investigated. In most cases, the lateral segment is connected to the basic mesogen by a functional group or by a spacer of different length [3,4].

Previous investigations on terminally branched molecules have shown that the introduction of perfluoroalkyl chains increases the phase transition temperatures and the tendency to form smectic phases [5]. Furthermore, the position of the fluorinated chain situated in these non-rod like molecules influences the polymorphism and the molecular packing significantly. These swallow-tailed substances as well as the laterally branched compounds can be defined as wedge-shaped mesogens. Therefore, in the present paper we want to clarify the question: Is there a similarly interesting behaviour of laterally aryl substituted molecules having perfluorinated chains? According to the design of laterally branched molecules, we created 4-hydroxybenzoic acid derivatives **A** and **B** with a ben-

zyl substituent in the branch. It is connected by a carboxylic group in the type **A**, but only by an oxygen in the type **B** compounds. Additionally, the dipoles of the carboxylic groups in **A** and **B** are directed opposite which is important for following miscibility studies.



A1



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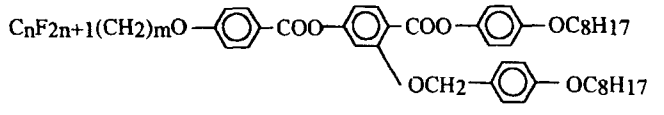


B

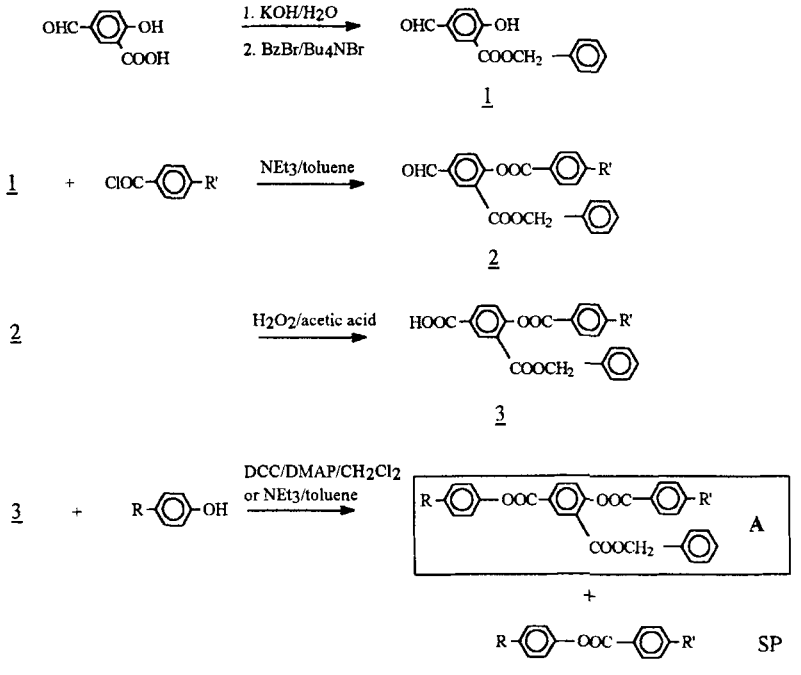
n=3,6,7,8,9,11; m=1,2

In the series **A**, we divided in two classes which differed in the position of the perfluoroalkylalkoxy chain in the smaller part (**A1**) or in the broader part (**A2**) of the wedge. The center of fluorination in the molecules **B** is in the small part of the wedge. ^{1}H- and ^{19}F-NMR were carried out to confirm the structures. The mesomorphic behaviour was investigated by polarization microscopy (Nikon Labophot 2A, hot stage: THMS 600 from Linkam) and differential scanning calorimetry (Perkin-Elmer-DSC 7).

SYNTHESIS

The synthesis of the type **A** compounds was carried out in 4 steps (Figure 1). The formation of the benzyl 2-hydroxy-5-formylbenzoate 1 through reaction of the potassium 2-hydroxy-5-formylbenzoate with benzyl bromide in the presence of tetrabutylammonium bromide proceeded in low yields of 10-20 % [6]. Esterification of 1 with the 4-substituted benzoylchorides [7] and oxidation of the formyl group with hydrogen peroxide lead to the 3-benzyloxycarbonyl-4-(4-subst.-benzoyloxy)benzoic acids 3. If R' is a perfluoroalkylalkoxy chain, the aldehydes 2 are liquid crystalline themselves. The existence of mesophases in these compounds is very surprisingly and will be discussed in a

special paper [9]. In the class of the benzoic acids 3 all derivatives show mesomorphic behaviour [8,9]. Final reaction with the 4-substituted phenoles [7] by means of DCC/ DMAP [9] or via the acid chloride of 3 with triethylamine produces the isophthalic acid derivatives **A1** and **A2**. They have to be purified by column chromatography using silica and chloroform or methylene chloride/light petroleum=5:1 as the eluent. This is needed because the removal of the liquid crystalline phenyl benzoates SP resulting as by-products (10-20% according to the phenol) is successfull only by this process. The formation of SP can be understood if the derivative 3 is regarded as an activated ester of the substituted benzoic acid where R'-Phenyl-CO cleaves and then reacts with the 4-substituted phenol. Hereby the part of the by-products is smaller by using DCC/DMAP for the esterification.



A1: R= $C_nF_{2n+1}(CH_2)_mO$; R'=OC_8H_{17}

A2: R= $C_8H_{17}O$; R'=$O(CH_2)_mC_nF_{2n+1}$

FIGURE 1 Scheme of the reaction pathway to synthesize the isophthalic acid derivatives.

Preparation of the type **B** substances was realized according to the pathway shown in Figure 2. The central moiety is the b-resorcylic acid. Protection of the two hydroxy groups is necessary for esterification of the carboxylic acid with 4-n-octyloxyphenol giving 5 in good yields. The deprotection is effected by hydrogenation with Pd/H_2 yielding 6. A regioselective reaction of one of the two hydroxy units is possible using DCC/DMAP for the esterification to the mesomorphic intermediates 7 [8]. Finishing etherification according to Mitsunobu [11] with 4-n-octyloxybenzylic alcohol produces the substances **B**.

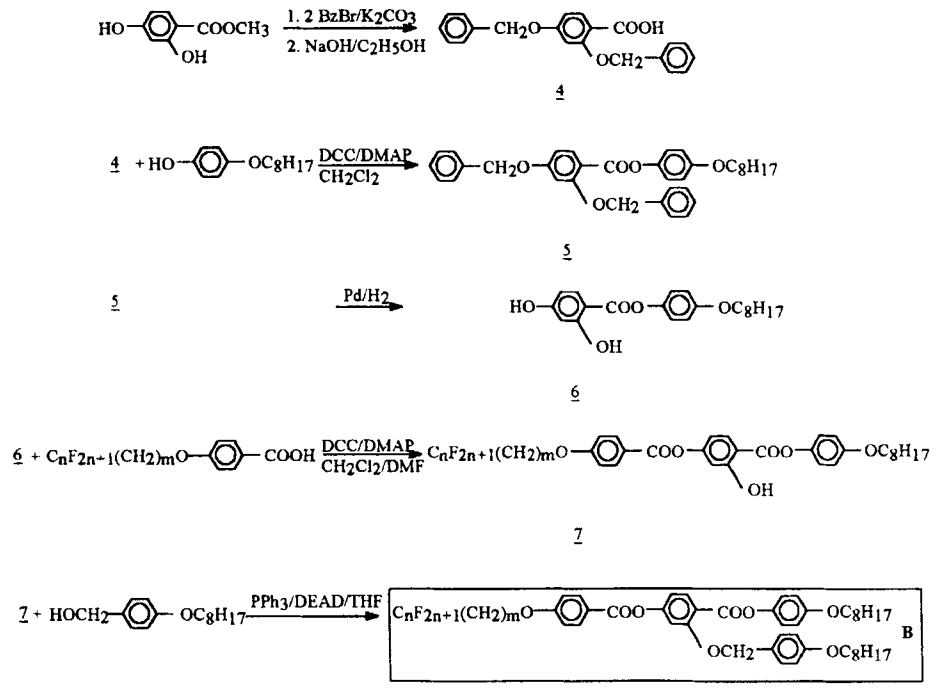


FIGURE 2 Reaction pathway to prepare the perfluorinated resorcylic acid compounds **B**.

MESOMORPHIC BEHAVIOUR

There are some similarities in the mesomorphic properties of the represented substances (see Table I-III). So the clearing points increase with incorporation of the fluorinated

alkyl chain compared to the nonfluorinated parent molecules. This tendency is verified by the phase behaviour of the two nonfluorinated reference substances: Comparing with the molecules **A1/2**, **A1/3**, **A2/2** and **A2/3** the nonfluorinated octyloxy derivative (n=0, m=8) exhibits the transition temperatures cr 91.5 (N 84) is. Exchange of the perfluorinated chain by an octyloxy group (n=0, m=8) in the compounds **B/2** and **B/3** yields the phase behaviour cr 73 (S_C 55) N 79 is. But the main feature is the disappearance of the nematic phase and the stabilization of the smectic phases in the type **A** and **B** compounds because the all-trans perfluoroalkyl chain leads to more rigid molecules. This is also the reason for the increase in the transition temperatures with lengthening of the chain from n+m=4 to 10 or 12. Often perfluorination results in higher melting points and a higher crystallization tendency. The opposite can be observed in the resorcylic acid derivatives **B** (Table III) where the recrystallization is greatly delayed and the smectic C phase is stable at room temperature for a few days. A glass transition could not detected by DSC. In the type **A** compounds only the molecules with two methylene units (m=2) possess a smectic C phase but also have lower clearing temperatures. The different position of the perfluorinated segment in the smaller part (**A1**) or in the broader part (**A2**) of the molecule has only a small effect on the height of the transition temperatures and none on the polymorphism in these two series.

TABLE I Transition temperatures for the type **A1** compounds.

no.	n	m	cr	lc[a]	S_C	S_A	is
A1/1	3	1	.96	-	-	(.88)	.
A1/2	6	2	.72	-	.(64)	.142.5	.
A1/3	7	1	.67	-	-	.156	.
A1/4	8	2	.81	-	.89.5	.171	.
A1/5	9	1	.74	(.41)	-	.179	.
A1/6	11	1	.83		-	.212	.

a. The liquid crystalline phase lc has not yet been determined exactly.

TABLE II Transition temperatures of the substances **A2**.

no.	n	m	cr	Ic	S_C	S_A	is
A2/1	3	1	.103	-	-	(.95)	.
A2/2	6	2	.106	-	(.69)	.147.5	.
A2/3	7	1	.101	-	-	.160	.
A2/4	8	2	.96	-	(.82)	.174	.
A2/5	9	1	.103	(.91)	-	.185	.

TABLE III Polymorphism of the resorcylic acid derivatives **B**.

no.	n	m	cr	S_C	S_A	is
B/1	3	1	.87	-	.102.5	.
B/2	6	2	.88	.108.7	.145	.
B/3	7	1	.80	.110.5	.143.5	.
B/4	8	2	.70	.136.5	.163	.
B/5	9	1	-	.126	.167	.

EXPERIMENTAL

Only the last step in the reaction pathway of the compounds **A1**, **A2** and **B** are reported in this paper. The homologues **A1/1-A1/3** are prepared according to method 1. The substances **A1/4-A1/6** and all compounds of the series **A2** are synthesized via method 2. Acting for all substances analytical data for one example of each series are given. A more detailed synthetic route and the liquid crystalline behaviour of the intermediates 2, 3 and 7 will be given in another paper [9].

Preparation of the laterally benzyloxycarbonyl substituted compounds A1/A2

Method 1:

0.6 mmol of the 4-substituted phenol and 0.72 mmol (0.1 ml) triethylamine are added slowly to a solution of 0.6 mmol 3-benzyloxycarbonyl-4-(4-subst.-benzoyloxy)benzoyl

chloride, prepared from the corresponding benzoic acid 3 by means of thionylchloride, in 50 ml dry toluene. The solution is stirred overnight at room temperature and after that 3 h at 60°C. After cooling the mixture is filtered through a short column of silica gel, the toluene is evaporated and the product is purified by column chromatography with silica and chloroform or methylene chloride/light petroleum=5:1 as the eluent. The first fraction contains the phenyl benzoates SP and the second the isophtalic acid derivatives **A1/1-A1/3** (yields: 17-30 %).

Method 2:

0.6 mmol of the corresponding 3-benzyloxycarbonyl-4-(4-subst.-benzoyloxy)benzoic acid 3, 0.63 mmol of the 4-subst.-phenoles, 0.64 mmol (0.13 g) DCC and catalytic amounts of DMAP are dissolved under stirring in 40 ml methylene chloride at room temperature. After one day the reaction is stopped in order to minimize the formation of the by-products SP. Removal of the solvent is followed by purification of the crude product by column chromatography as described in method 1 yielding the products **A1/4-A1/6** (yields: 30-38 %) and **A2/1-A2/5** (yields: 29-40 %).

A1/4: ^{1}H-NMR ($CDCl_3$, TMS): d = 0,84-0,87 (m, 3H, CH_3), 1,23-1,85 (m, 12H, 6·CH_2), 2,53-2,72 (m, 2H, $OCH_2CH_2C_8F_{17}$), 3,99-4,06 (t, 2H, OCH_2), 4,23-4,3 (t, 2H, $OCH_2CH_2C_8F_{17}$), 5,21 (s, 2H, $COOCH_2Ar$), 6,87-8,87 (m, 15H, arom. H); ^{19}F-NMR ($CDCl_3$, CF_3COOH): d = -81,01 - -81,06 (s, 3F, CF_3), -113,36 - -113,49 (m, 2F, $OCH_2CH_2CF_2C_7F_{15}$), -121,81 - -126,32 (m, 12F, 6·CF_2)

A2/5: ^{1}H-NMR ($CDCl_3$, TMS): d = 0,83-0,87 (m, 3H, CH_3), 1,29-1,8 (m, 12H, 6·CH_2), 3,91-3,97 (t, 2H, OCH_2), 4,48-4,61 (t, 2H, $OCH_2C_9F_{19}$), 5,21 (s, 2H, $COOCH_2Ar$), 6,89-8,89 (m, 15H, arom. H); ^{19}F-NMR ($CDCl_3$, CF_3COOH): d = -80,99 - -81,03 (s, 3F, CF_3), -119,43 - -119,45 (m, 2F, $OCH_2CF_2C_8F_{17}$), -121,91 - -126,28 (m, 14F, 7·CF_2)

Preparation of the 4-n-octyloxyphenyl 2-(4-n-octyloxybenzyloxy)-4-(4-perfluoroalkyl-alkoxybenzoyloxy)benzoates ***B***

0.23 mmol of a 4-n-octyloxyphenyl 2-hydroxy-4-(4-perfluoroalkylalkoxybenzoyl-oxy)benzoate 7 and 0.35 mmol (0.08 g) 4-n-octyloxybenzylic alcohol are dissolved in 50 ml dry THF under nitrogen at 0°C. 0.27 mmol (0.07 g) triphenylphosphine and 0.27 mmol (0.04 ml) diethyl azodicarboxylate are added slowly under stirring. The reaction

is stopped if none phenol is detectable by thin-layer chromatography. The solvent is evaporated and the precipitate is purified by recrystallization from ethanol/toluene for **B1** and **B2** (yields: 63 and 72 % resp.), ethanol for **B3** and **B4** (yields: 32 and 54 % resp.) or by column chromatography with silica gel and methylene chloride/light ether=5:1 as eluent for **B5** (yield: 10 %).

B2: ^{1}H-NMR ($CDCl_3$, TMS): d = 0,84-0,89 (m, 6H, 2·CH_3) , 1,18-1,83 (m, 24H, 12·CH_2), 2,58-2,8 (m, 2H, $OCH_2CH_2C_6F_{13}$), 3,88-3,96 (m, 4H, 2·OCH_2), 4,33-4,39 (t, 2H, $OCH_2CH_2C_6F_{13}$), 5,11 (s, 2H, OCH_2Ar), 6,81-8,18 (m, 15H, arom. H);
^{19}F-NMR ($CDCl_3$, CF_3COOH): d = -81,03 - -81,07 (s, 3F, CF_3), -113,36 - -113,49 (m, 2F, $OCH_2CH_2CF_2C_5F_{11}$), -122,03 - -126,35 (m, 8F, 4·CF_2)

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