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C. Stützer [a] & W. Weissflog [a]

[a] Max-Planck-Gesellschaft, Arbeitsgruppe "Flüssigkristalline Systeme", Mühlpforte 1, D-06108, Halle, Germany

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In Search of Smectic C Phases at Mesogens with a Phenyl Ring Containing Lateral Branch

C. STÜTZER and W. WEISSFLOG

Max-Planck-Gesellschaft, Arbeitsgruppe "Flüssigkristalline Systeme", Mühlpforte 1, D-06108 Halle, Germany

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Generally, substituents laterally attached at calamitic molecules prevent the existence of tilted smectic phases. However, mesogens with a bulky phenyl ring containing lateral branch are subjected to other relationships. The following constitutional parameters should be realized to prepare liquid crystals exhibiting smectic C* phases: the lateral aromatic ring is linked by an odd-numbered spacer to a four-ring basic molecule bearing the chiral group. The lateral phenyl ring should be substituted in 4-position with substituents having a suitable shape and defined electron-withdrawing properties. Biphenyl units within the basic mesogen are of advantage. Measurements of the spontaneous polarization were performed. Therefore, by the existence of one chloro or nitro substituent in ortho-position to the chiral 1-methylheptyloxy group the values of P_s are increased. However, the bulky lateral segment is of few influence on the spontaneous polarization.

Keywords: Nonconventional liquid crystals; bulky branched mesogens; smectic C phases; smectic C* phases; spontaneous polarization

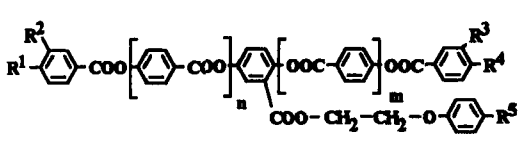
1. INTRODUCTION

Thermotropic liquid crystals with a molecular shape deviating from the rod-like or disc-like one often show an unexpected mesogenic behaviour. Thus, the influence of lateral long-chain substituents on the mesophase behaviour of three-ring compounds has been discussed manifold [1–4]. All these substances prefer to form nematic phases. In homologous series the clearing temperatures decrease with increasing length of the lateral alkyl chains tending towards convergence temperatures.

In contrary to former informations the existence of aromatic, cycloaliphatic or heterocyclic rings in a lateral position of three-ring mesogens do not cause the loss of liquid crystalline properties [5–8]. The clearing temperatures are unexpectedly high if the lateral ring system is linked to the basic mesogen by means of a flexible and odd numbered spacer. As proved by X-ray studies [9–11] the lateral segments are oriented in direction of the long axes of the basic molecules.

Mesogens with such a bulky lateral group favour an antiparallel ordering to reach a high packing density. The lateral phenyl ring can be substituted itself in a versatile manner. Type and position of the substituents are of influence on the polymorphism. Unbranched groups attached in para-position initiate an increase of the clearing temperatures. Strongly electron-withdrawing substituents, like the cyano or nitro group, preferably lead to substances with smectic A phases. Mesogens with other groups, e.g. alkyloxy, alkyl, halogenes, at the laterally linked aromatic ring can exhibit smectic C phases below the nematic ones, but almost on supercooling, only [5, 6].

Because of the continuous interest in liquid crystals with smectic C phases and S_C*-phases, e.g. for ferroelectric investigations, in the present paper we discuss the existence of tilted phases in mesogens with a bulky lateral segment having the following structure:



6 - 8

The new substances are characterized by a three- or four-ring basic mesogen with one substituted phenyl ring in a lateral position linked by a five-numbered spacer together. Variation of the chemical constitution by changing the length of the basic mesogen, by different substituents R^1–R^5, but also by removing of one carboxylic unit by using biphenyl carboxylic acids, will offer ways to produce compounds with enantiotropic smectic C phases. Introduction of chiral groups within selected derivatives should yield S_C*-phases.

Different constitutional parameters affect the spontaneous polarization, for instance the number and power of dipols situated close to or at the chiral centre [12–14]. Now, the question arises wether bulky lateral segments are of influence on the spontaneous polarization by steric hindrance.

2. SYNTHESIS

The reaction path to prepare the compounds under discussion is shown in Figure 1. After protection of the phenolic groups of gentisic acid by means of benzyl ethers the intermediate **1** was esterificated with 2-(4-*n*-nonanoylphenoxy)ethanol **2** to produce **3a**. Deprotection realized by hydrogenolysis yielded 2-(4-nonanoylphenoxy)ethyl 2,5-dihydroxybenzoate **4a**. The dihydroxy derivative **4a** can be esterificated regioselectively in 5-position with appropriate benzoic acids by using DCC/DMAP [15] to give the half-esters **5**. Second acylation with substituted benzoyl chlorides produced the substances **6**–**8**.

Using substituted 4-benzoyloxybenzoic acids (n or $m = 1$) in the first or second step of esterification yields the compounds having a four ring basic

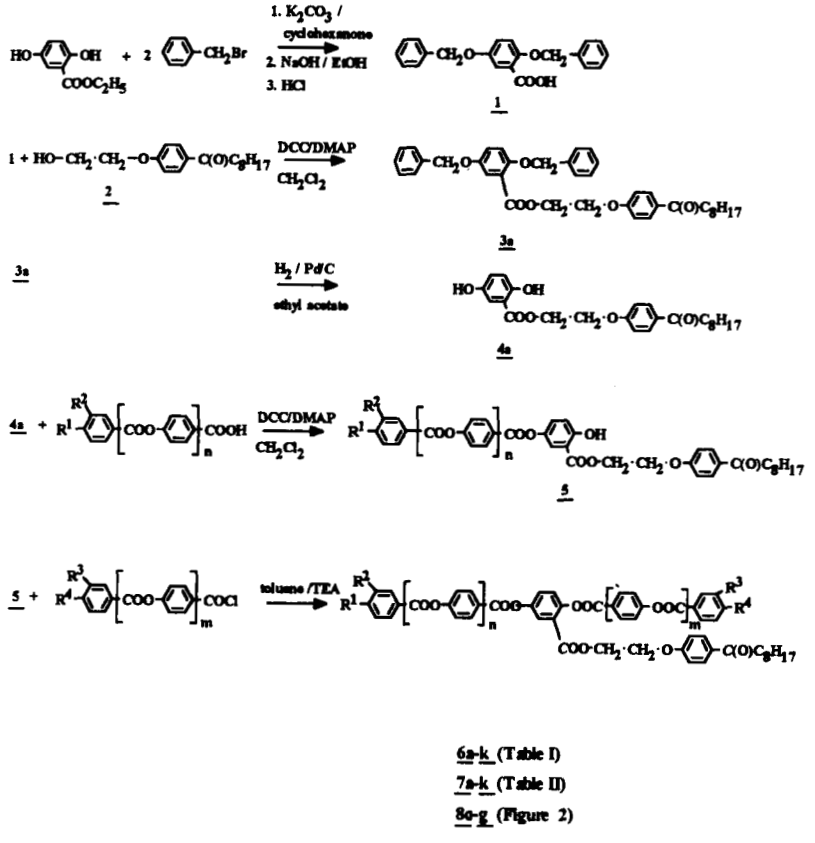
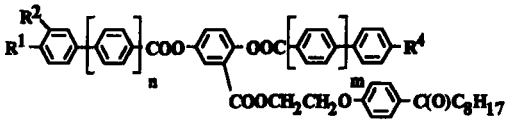


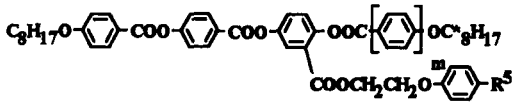
FIGURE 1 Reaction path to prepare nonsymmetrical 2,5-disubstituted benzoic acid derivatives.

mesogen. Reaction with substituted biphenylcarboxylic acids in one step of acylation produces substances **9**, the number of connecting groups is reduced by one carboxylic unit.



9: $R^1, R^4 = C_8H_{17}O, C^*_8H_{17}O$; $R^2 = H, Cl$; $m, n = 0, 1$

The reaction pathway described can be used generally to prepare unsymmetrically disubstituted gentisic esters. E.g., by esterification of the 4-tert.-butyl- or 4-*n*-hexyloxycarbonyl-phenoxyethanol, respectively, with the protected gentisic acid **1** and further reactions as shown in Figure 1 the corresponding substances **10** and **11** have been synthesized.



10: $R^5 = COOC_6H_{13}$, $m = 1$ or 2

11: $R^5 = C(CH_3)_3$, $m = 1$ or 2

3. RESULTS AND DISCUSSION

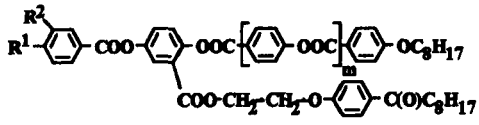
3.1. Mesophase Behaviour

The stable smectic C phase (persistence range 19 K) of the symmetric disubstituted derivative **6a** has been the starting point of our investigation [6]. Introduction of a chiral centre should give substances exhibiting a S_C^* phase wanted. But, as shown in the Tables I and II, appropriate variations of substituents at the three-ring compounds ($m = 0$) result in a depression of smectic C phases. For all the substances having a branched optically active group the S_C^* phase could not be detected.

Now, the length of the basic mesogens was increased. The corresponding four-ring compounds **6** and **7** are isomeric one to another and differ in the position of linking of the lateral segment. This alteration is of influence on the molecular shape and, therefore, should affect the package of molecules in the liquid crystalline state.

As expected, all the derivatives containing a four-ring basic compound **6**, **7** (m or $n = 1$) show the higher clearing temperatures. In the Tables I and II the mesophase behaviour of the three-ring and four-ring compounds can be compared one to another. Lengthening of the basic mesogens can result in a stabilization of tilted phases. However, the effect is depending strongly on the direction of the lateral segment. Only the chiral compounds **6** exhibit

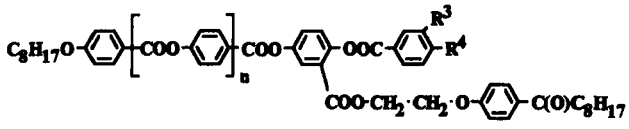
TABLE I Transition temperatures of the compounds **6**



no.	R^1	R^2	*m*	*Cr*	S_C/S_C^*	S_A	*N/Ch*	*Is*
6a [6]	$C_8H_{17}O$	H	0	.121	.140	.144	-	.
6b	$C_8H_{17}O$	H	1	.133	.165	-	.193	.
6c	$C_8H_{17}O$	Cl	0	.111	(.96	-	.97)	.
6d	$C_8H_{17}O$	Cl	1	.86	.117	-	.159	.
6e	$C^*_5H_{11}O$	H	0	.135	-	(.133)	-	.
6f	$C^*_5H_{11}O$	H	1	.141	.145	-	.186	.
6g	$C^*_8H_{17}O$	H	0	.121	-	(.113)	-	.
6h	$C^*_8H_{17}O$	H	1	.118	.141	-	.160	.
6i	CN	H	0	.111	-	.153	-	.
6k	CN	H	1	.120	-	.179	.205	.

$C^*_5H_{11}O = C_2H_5C^*H(CH_3)CH_2O$
$C^*_8H_{17}O = C_6H_{13}C^*H(CH_3)O$

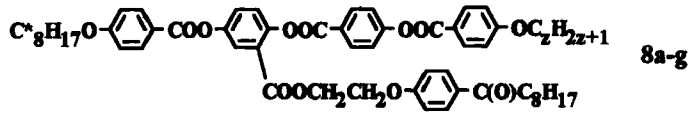
TABLE II Transition temperatures of the compounds **7**



no.	R^3	R^4	*n*	*Cr*	S_C/S_C^*	S_A	*N/Ch*	*Is*
7a [6]	H	OC_8H_{17}	0	.121	.140	.144	-	.
7b	H	OC_8H_{17}	1	.112	.119	-	.180	.
7c	Cl	OC_8H_{17}	0	.108	(.97	-	.98)	.
7d	Cl	OC_8H_{17}	1	.110	.156	-	.180	.
7e	H	$OC^*_5H_{11}$	0	.109	-	.119	.124	.
7f	H	$OC^*_5H_{11}$	1	.112	(.111)	-	.189	.
7g	H	$OC^*_8H_{17}$	0	.110	-	-	-1)	.
7h	H	$OC^*_8H_{17}$	1	.86	(.76)	-	.136	.
7i	H	CN	0	.132	-	.168	-	.
7k	H	CN	1	.123	-	.226	-	.

[1] Liquid crystalline phase below 96°C, type of mesophase could not be determined.

enantiotropic S_C^* phases persistent enough for further measurements. Therefore, a homologous series **8** was prepared, which is derived from **6h**, see Figure 2. The clearing points of the homologues exist in a near temperature range. Some of the new substances have phase ranges suitable for following investigations.



8a-g

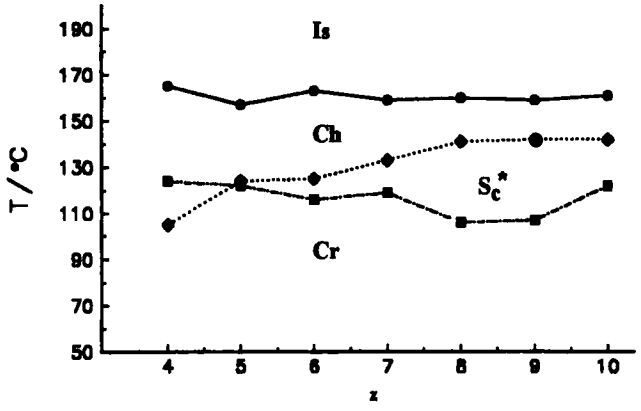


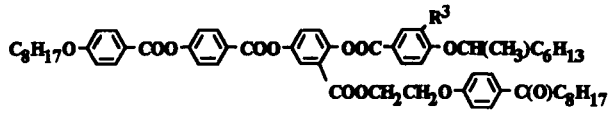
FIGURE 2 Phase transition temperatures of the homologous series **8a–g**.

Substitution of one terminal position of the basic mesogen by a cyano group results in high clearing points, but in a loss of tilted phases (**6i, k** and **7i, k**). Such a dominance of orthogonal phases has been described for laterally 4-cyano- or 4-nitrobenzyl substituted esters of gentisic acid, too [11].

The phase behaviour given in the Tables I and II show that the influence of a chloro group in R^2 or R^3 on the clearing temperatures as well as on the stability of the smectic C phase can be very different, depending on the length of the basic molecules, the positions of the additional substituent and of the lateral segment. To transfer the results to chiral derivatives, the compounds **7l** and **7m** have been synthesized. In these molecules three branches are situated on one side of the mesogens: the 2-octyloxy group, the bulky lateral segment and the substitutent R^3. As shown in Table III, the clearing points are not depressed by the lateral group R^3, but the stability of the S_C* phase is increased. 3-Nitro-4-(1-methyl-heptyloxy)benzoates, like **7m**, show a clear tendency to produce glassy mesophases, as also reported by Heppke *et al.*, recently [8].

Biphenyl units situated in rod-like mesogens often support the existence of smectic phases. The question arises wether the same tendency can be observed for laterally branched compounds. The biphenyl derivatives **9** have a higher mesophase stability than the corresponding four-ring compounds **6** and **7** and exhibit a changed polymorphism. Smectic phases are stabilized, see Table IV. It is important to know that the simultaneous existence of the

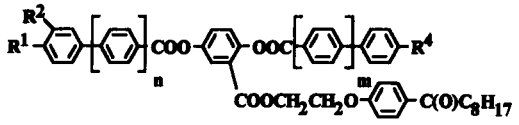
TABLE III Threefold branched mesogens exhibiting S_C^* phases



no.	R^3	*Cr*	S_C^*	*Ch*	*Is*
7h	H	.86	(.76)	.136	.
7l	Cl	.70	.111	.138	.
7m	NO_2	.26[Tg]	.115	.140	.

[Tg] Glass transition temperature

TABLE IV Transition behaviour of the biphenyl derivates **9**



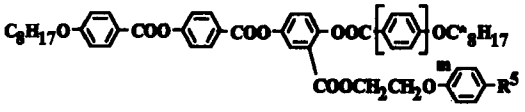
no.	R^1	R^2	R^4	*n*	*m*	*Cr*	S_C/S_C^*	S_A	*N/Ch*	*Is*
9a	$C_8H_{17}O$	H	OC_8H_{17}	0	1	.147	.194	.202	.204	.
9b	$C_8H_{17}O$	H	$OC^*_8H_{17}$	0	1	.139	.163	.165	.168	.
9c	$C_8H_{17}O$	Cl	$OC^*_8H_{17}$	0	1	.121	(.109	-	.120)	.
9d	$C^*_8H_{17}O$	H	OC_8H_{17}	1	0	.142	.152	.154	.160	.
9e	$C^*_8H_{17}O$	H	$OC^*_8H_{17}$	0	1	.144	-	(.142)	-	.
9f	$C^*_8H_{17}O$	H	$OC^*_8H_{17}$	1	1	.165	-	.177	.189	.

branched 1-methylheptyloxy chains at both terminal positions of the basic mesogens prevents the formation of tilted phases, as shown at the four-ring **9e** as well as the five-ring compound **9f**.

In previous papers [5, 6] we have reported the effect of both the type and the number of substituents attached at the lateral phenyl ring. The enlargement of the bulkiness of the branch by multiple substitution or the use of polynuclear aromatics in lateral position is possible without loss of the liquid crystalline properties. Herein, we have tested besides the nonanoyl group two other substituents, tert.-butyl and hexyloxycarbonyl in R^5, with the aspect of formation of smectic C phases. The mesophase behaviour of the compounds **10** and **11** is listed in Table V.

Only alkyloxycarbonyl groups, but not the tert.-butyl group, are suitable to produce tilted phases in the substance class under investigation. In our

TABLE V The influence of the substituents R^5 attached at the lateral phenyl ring on the mesophase behaviour



10, 11; m = 1 or 2

no.	R^5	*m*	*Cr*	S_C*	S_A	*Ch*	*Is*
10a	$COOC_6H_{13}$	1	.105	(.84)	-	.144	.
10b	$COOC_6H_{13}$	2	.109	.130	-	.217	.
11a	$C(CH_3)_3$	1	.108	-	-	.125	.
11b	$C(CH_3)_3$	2	.140	(.112)	-	.214	.

opinion, the shape and the right level of electron-withdrawing properties of these substituents attached in the para-position R^5 are of a great importance. However, strongly electron-accepting groups, like cyano or nitro, prevent the formation of smectic C phases.

3.2. Molecular Structure and Spontaneous Polarization

The ferroelectric polarization was measured by the triangular wave method [16] in 10 μm cells with indium tin oxide (ITO) electrodes coated with polyimide (EHC, Japan). The temperature dependence of the spontaneous polarization plotted versus $T\text{-}T_{SC^*/Ch}$ of four homologues of series **8** is shown in Figure 3a. The behaviour typically for a first order phase transition has been often reported for Ch-S_C* materials [17, 18]. The values of Ps measured 10 degrees below the transition cholesteric - smectic C* are from 20 up to 60 $nC\,cm^{-2}$. Therefore, clearly higher polarization due to the bulky lateral segments do not occur. Within the homologous series **8c–g** the polarization decreases with lengthening of the terminal alkyloxy chain R^4 (Fig. 3a). For rod-like substances often the polarization is the greater if the chain attached to the chiral centre being longer [17, 18]. The dependence of the tilt angles, resulted from the switching measurements, from the temperature is shown in Figure 3b.

To compare the spontaneous polarization in relation to the constitution of the mesogens angle-independent values P_O are calculated and summarized in Table VI. Therefore, the influence of the chain length in the terminal position R^4 is unusually great. With shortening the alkyloxy group the spontaneous polarization increase clearly. However, the value P_O for the

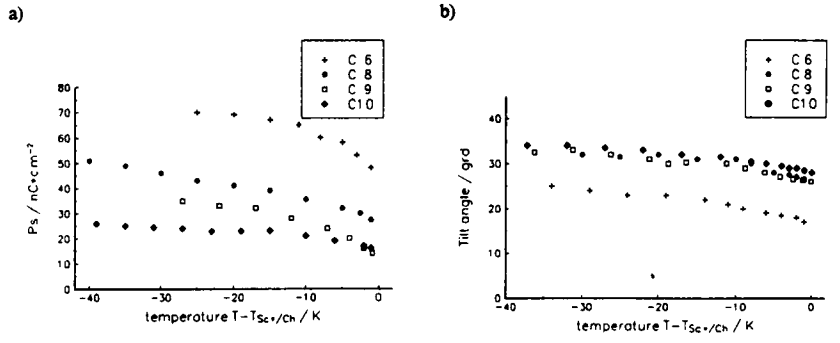


FIGURE 3 a) Spontaneous polarization and b) tilt angle of four derivatives of the homologous series **8** versus $T\text{-}T_{SC^*/Ch}$.

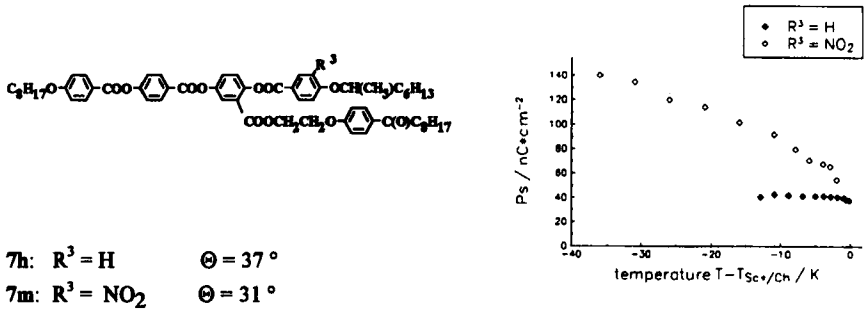
hexyloxy derivative **8c** is situated very high. This could be because of an intercalation effect of the terminal alkyl chains within the package of mesogens having such nonconventional molecular shape. Unfortunately, the homologes **8a–b** having shorter alkyloxy chains could not be investigated because of a very high crystallization tendency. The relationships under discussion should be the aim of further investigations

Introduction of the nitro group in ortho-position to the branched alkyloxy chain produces a higher spontaneous polarization, as seen in Figure 4. The value of P_O: 178.6 nC cm^{-2} for compound **7m** in comparison to the unsubstituted derivative **7h** (P_O: 64.8 nC cm^{-2}) is caused by increasing the transversal dipol moment. The remarkable effect of nitro substitution ortho to the chiral group on the spontaneous polarization has been already reported by Walba *et al.* [19] and Zentel *et al.* [20]. Similar growing of the spontaneous polarization was found for ortho-cyano substituted rod-like derivates [21].

The chiral 1-methylheptyloxy group can be located close to the bulky lateral segment or at the other terminal end of the basic mesogen. To check the relationships between these different constitution and P_S two corresponding

TABLE VI Comparison of the spontaneous polarization within the homologous series **8**

no.	*z*	*tilt angle* Θ	P_S *(nC/cm²)*	P_0 *(nC/cm²)*
8c	6	20	61.0	178.3
8e	8	31	36.9	71.8
8f	9	29	26.3	54.2
8g	10	31	24.1	46.8

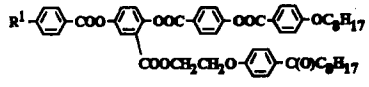


7h: $R^3 = H$ $\Theta = 37°$
7m: $R^3 = NO_2$ $\Theta = 31°$

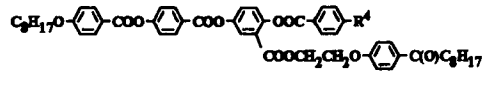
FIGURE 4 Effect of a nitro substituent in R^3 on the spontaneous polarization.

pairs of isomeric compounds were investigated. In the following the formula of the substances ($R^1, R^4 = C_8H_{17}$*O) under discussion are shown.

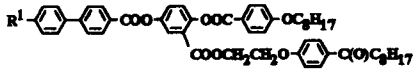
6h



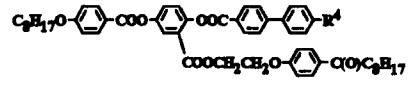
7h



9d



9b



As given in Table VII the differences of P_0 between the isomeric compounds **6h** and **7h** as well as **9d** and **9b** are very small. The substances containing biphenyl exhibit the higher values. Apparently, the distance of the bulky lateral 2-(4-*n*-nonanoylphenoxy)ethyloxycarbonyl segment from the optically active centre has few influence on the spontaneous polarization, only. Contrary, mesogens having the chiral branch at position R^1 (**6h** and **9d**) possess a little higher values P_0 in comparison to **7h** and **9b**. This demonstrates that

TABLE VII Camparison of the spontaneous polarization of two isomeric pairs

no.	*tilt angle* Θ	P_S *(nC/cm²)*	P_0 *(nC/cm²)*
6h	31	36.9	71.8
7h	37	42.0	69.8
9d	24.5	23.5	104.6
9b	13	42.7	101.7

the hindrance of the free rotation of the perpendicular dipol is not influenced by the lateral branch or in other words, the lateral group can be regarded as an independent molecular segment with respect to the production of P_O.

4. CONCLUSIONS

Lateral substitution of the middle phenyl ring of three-ring mesogens by small or long-chain groups prevents the formation of smectic C phases. By insertion of an aromatic ring within the lateral segment the structure-mesophase relationships are changed strikingly. Using an odd-numbered spacer these mesogens with a phenyl ring containing lateral branch can exhibit layer structures. However, the tilted smectic phases existing in laterally 4-nonanoyl-phenoxyethoxycarbonyl substituted three-ring compounds disappear if the basic mesogen is provided with a chiral wing group. Lengthening of the basic mesogen by a further phenyl ring proved to be of advantage. Position and direction of the lateral segment attached to the basic mesogen are of importance to synthesize compounds having stable S_C* phases. Polar groups, like chlorine or nitro, linked in ortho position to the optically active, terminal chain, support the stability of smectic C* phases without depression of the clearing points. Biphenyl units within the basic mesogens stabilize the persistence range of tilted phases in comparison to the benzoyloxyphenyl fragments. According to the results known yet, weakly electron-withdrawing properties of the substituents attached at the lateral phenyl ring stimulate the formation of S_C* phases, but strong electron-accepting groups, like cyano or nitro, support the existence of S_A phases.

It should be emphasized once more that the existence of smectic C phases in laterally branched mesogens is rare. Usually, lateral substituents depress the tendency to form layer structures much more than the nematic phases. According to results recently published by Tschierske *et al.* [22] additional hydroxylic groups located at lateral alkyl chains are able to support the formation of smectic A phases, but not of smectic C phases.

Measurements of the spontaneous polarization of selected compounds do not show unusual behaviour. The values of p_s have the same magnitude independent of the direction of the lateral substituent. Therefore, the neighbourhood of the chiral centre and the bulky lateral segment is not of a great influence on the spontaneous polarization. The results support that view therefore it is the rotational trapment of the chiral centre itself plus the

coupling to the local dipolar environment that yields spontaneous polarization, i.e., the molecular shape and molecular dipole have less importance in determining the size of the polarization.

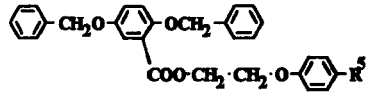
5. EXPERIMENTAL

The purity of the new compounds was checked by elemental analysis, HPLC, ^{1}H-NMR, and mass spectroscopy. ^{1}H-NMR spectra were recorded on the spectrometers "Unity 500" (Varian) and a "WP 200" (Bruker) using $CDCl_3$ as solvent and tetramethylsilan as internal standard, δ in ppm. Mass spectra were recorded on an AMD 402 (70 eV) mass spectrometer (Intecta GmbH). Optical rotation were measured using a polarimeter type "polartronic-D" (Schmidt-Haensch). Calorimetric measurements were carried out using differential scanning calorimetry (Perkin-Elmer DSC 7). The transition temperatures were determined using a polarizing microscope (Nikon Optiphot-2) in combination with a hot stage THM 600/S and the temperature control unit TP 92.

2,5-Dibenzyloxybenzoic acid **1** [23], 2-(4-subst.-phenoxy)ethanols **2** (**2a** $R^5 = C(O)C_8H_{17}$, **2b** $R^5 = COOC_6H_{13}$, **2c** $R^5 = C(CH_3)_3$) [24] and the substituted benzoic acids were synthesized according to well-known procedures.

5.1. 4-Subst.-phenoxyethyl 2,5-dibenzyloxybenzoates 3

25 mmol (9.05 g) 2,5-dibenzyloxybenzoic acid **1**, 25 mmol of the appropriate compound **2**, 30 mmol (6.18 g) *N*, *N'*-dicyclohexylcarbodiimide and a catalytic amount of dimethylaminopyridine in 100 ml dry dichloromethane were stirred overnight. The solvent was removed and the residue was recrystallized from cyclohexane. Yields 55–73%

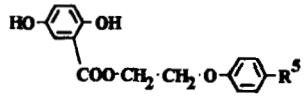


no.	R^5	mp. (°C)	molecular formula	elemental analysis (%) (calcd./found) C	H
3a	$C(O)C_8H_{17}$	70	$C_{38}H_{42}O_6$ (594.75)	76.73/ 76.55	7.12/ 7.08
3b	$COOC_6H_{13}$	65	$C_{36}H_{38}O_7$ (582.69)	74.19/ 74.24	6.58/ 6.62
3c	$C(CH_3)_3$	115	$C_{33}H_{34}O_5$ (510.63)	77.61/ 77.73	6.72/ 6.60

3a ^{1}H-NMR: 0.84 (t, 3H, CH_3); 1.10–1.50 (m, 10H, 5 × CH_2); 1.62–1.90 (m, 2H, C(O)CH_2CH_2); 2.85 (t, 2H, J = 7.1 Hz, C(O)CH_2); 4.26 (t, 2H, J = 4.7 Hz, OCH_2), 4.20 and 5.04 (s, 4H, OCH_2); 4.61 (t, 2H, J = 4.8 Hz, $COOCH_2$); 6.80–7.05 (m, 2H, H-ar); 7.33–7.50 (m, 14H, H-ar); 7.9 (d, 1H, H-ar); MS: m/z 594 [M^+]

5.2. 4-Subst.-phenoxyethyl 2,5-dihydroxybenzoates 4

25 mmol compound **3**, 0.6 g catalyst (5% palladium on carbon), 200 ml ethyl acetate and 20 ml acetic acid were deprotected with hydrogene in a shaking bottle (standard pressure) until TLC analysis revealed the completeness of the reaction. The mixture was filtered off and the solvent evaporated. The residue was recrystallized from cyclohexane. Yields: 60–83%.



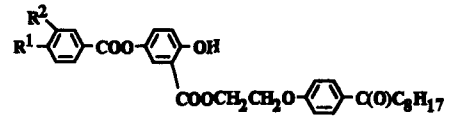
no.	R^5	mp. (°C)	molecular formula	elemental analysis (%) (calcd./ found)	
				C	H
4a	$C(O)C_8H_{17}$	93	$C_{24}H_{30}O_6$ (414.50)	69.53/ 69.32	7.30/ 7.35
4b	$COOC_6H_{13}$	75	$C_{22}H_{26}O_7$ (402.44)	65.66/ 65.48	6.51/ 6.55
4c	$C(CH_3)_3$	150	$C_{19}H_{22}O_5$ (330.38)	69.07/ 68.93	6.71/ 6.67

4a ^{1}H-NMR: 0.85 (t, 3H, J = 6.4 Hz, CH_3); 1.24–1.52 (m, 10H, 5 × CH_2); 1.55–1.58 (m, 2H, C(O)CH_2CH_2); 2.53 (t, 2H, J = 7.6 Hz, C(O)CH_2); 4.26 (t, 2H, J = 4.7 Hz, OCH_2), 4.63 (t, 2H, J = 4.7 Hz, $COOCH_2$); 6.81–6.87 (m, 2H, H-ar); 6.97 (d, 2H, H-ar); 7.11 (d, 2H, H-ar); 7.25 (d, 1H, H-ar); 10.21 (s, 1H, OH, ortho to COO); MS: m/z = 414 [M^+]

5.3. 4-Subst.-phenoxyethyl 2-hydroxy-5-(4-subst.-benzoyloxy) benzoates 5

The reaction was carried out using procedure described for the preparation of compounds **3** starting from 25 mmol of compound **4** and 25 mmol 4-substituted benzoic acids. Recrystallization from ethanol. Yields: 40–75%.

5a ^{1}H-NMR: 0.82–0.87 (m, 6H, 2 × CH_3); 1.24–1.44 (m, 20H, 10 × CH_2); 1.48–1.83 (m, 4H, C(O)CH_2CH_2, OCH_2CH_2); 2.85 (t, 2H, J = 7.4 Hz, C(O)CH_2); 4.01 (t, 2H, J = 6.5 Hz, OCH_2); 4.34 (t, 2H, J = 4.7 Hz,

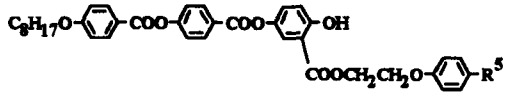


5a-5e

no.	R^1	R^2	mp. (°C)	molecular formula	elemental analysis (%) (calcd./found) C	H	Cl/N
5a	$C_8H_{17}O$	H	96	$C_{39}H_{50}O_8$ (646.82)	72.42/ 72.46	7.79/ 7.85	-
5b	$C_8H_{17}O$	Cl	52	$C_{39}H_{49}ClO_8$ (681.27)	68.79/ 68.96	7.26/ 7.43	5.14/ 5.10
5c	$C^*_5H_{11}O$	H	80	$C_{36}H_{44}O_8$ (604.74)	71.49/ 71.30	7.34/ 7.32	-
5d	$C^*_8H_{17}O$	H	94	$C_{39}H_{50}O_8$ (646.82)	72.42/ 72.50	7.79/ 7.52	-
5e	NC	H	95	$C_{32}H_{33}NO_7$ (543.62)	70.69/ 70.95	6.12/ 6.24	2.58/ 2.33

OCH_2); 4.69 (t, 2H, J = 4.6 Hz, $COOCH_2$); 6.81–8.10 (m, 11H, H-ar); 10.55 (s, 1H, OH); MS: m/z = 646 [M^+]

no.	R^5	mp.
5f	$C(O)C_8H_{17}$	102
5g	$COOC_6H_{13}$	85
5h	$C(CH_3)_3$	104



5f ^{1}H-NMR: 0.82–0.87 (m, 6H, 2 × CH_3); 1.23–1.48 (m, 20H, CH_2); 1.52–1.55 (m, 4H, $C(O)CH_2CH_2$, OCH_2CH_2); 2.49 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 4.26 (t, 2H, OCH_2); 4.34 (t, 2H, OCH_2); 4.67 (t, 2H, $COOCH_2$); 6.79–8.29 (m, 15H, H-ar); 10.63 (s, 1H, OH, ortho to COO); Elemental analysis (%): $C_{46}H_{54}O_{10}$ (766.93), (calcd./found) C: 72.03/72.23, H: 7.10/7.17

5.4. 4-Subst.-phenoxyethyl 2,5-bis (4-subst.- benzoyloxy) benzoates 6–11

To a solution of 10 mmol of the derivative **5** selected, 12 mmol (1.2 g) triethylamine in 50 ml dry toluene 10 mmol of the appropriate substituted benzoylchloride (if necessary a solution in toluene) was given dropwise at room temperature. The mixture was stirred overnight (exclusion of moisture) and after then, heated for 2–3 hours. The solvent was evaporated in vacuo. The residue was dissolved in dichloromethane, washed with water and a solution of sodium hydrogene carbonate. The organic solution was dried by means of anhydrous Na_2SO_4. After evaporation the residue was

recrystallized from ethanol/toluene or amyl alcohol to give substances **6–11**. Yields: 45–79%.

6a ^{1}H–NMR: 0.82–0.88 (m, 9H, 3 × CH_3); 1.24–1.49 (m, 30H, 15 × CH_2); 1.60–1.84 (m, 6H, 2 × OCH_2CH_2, $C(O)CH_2CH_2$); 2.48 (t, 2H, $C(O)CH_2$); 4.00–4.06 (m, 6H, 3 × OCH_2); 4.49 (t, 2H, $COOCH_2$); 6.63–8.18 (m, 15H, H-ar)

6b ^{1}H-NMR: 0.82–0.87 (m, 9H, 3 × CH_3); 1.24–1.50 (m, 30H, 15 × CH_2); 1.63–1.84 (m, 6H, 2 × OCH_2CH_2, $C(O)CH_2CH_2$); 2.80 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 4.00–4.07 (m, 6H, 3 × OCH_2); 4.54 (t, 2H, J = 4.6 Hz, $COOCH_2$); 6.73–8.22 (m, 19H, H-ar)

6c ^{1}H-NMR: 0.81–0.87 (m, 9H, 3 × CH_3); 1.19–1.49 (m, 30H, 15 × CH_2); 1.75–1.90 (m, 6H, 2 × OCH_2CH_2, $C(O)CH_2CH_2$); 2.48 (t, 2H, J = 7.6 Hz, $C(O)CH_2$); 3.91–3.98 (m, 4H, 2 × OCH_2); 4.10 (t, 2H, J = 6.6 Hz, OCH_2); 4.47 (t, 2H, J = 4.9 Hz, $COOCH_2$); 6.61–8.20 (m, 14H, H-ar)

6d Elemental analysis (%): $C_{61}H_{73}ClO_{12}$ (1033.70), (calcd./found): C: 70.90/71.02; H: 7.13/7.18; Cl: 3.39/3.29

6e ^{1}H-NMR: 0.84–0.98 (m, 9H, 3 × CH_3); 1.01–1.04 (d, 3H, $CH(CH_3)$); 1.21–1.48 (m, 22H, 11 × CH_2); 1.57–1.91 (m, 5H, OCH_2CH_2, $OCH_2CH(CH_3)$, $C(O)CH_2CH_2$); 2.86 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.83 (t, 2H, OCH_2); 3.89–4.04 (m, 4H, 2 × OCH_2); 4.51 (t, 2H, J = 4.8 Hz, $COOCH_2$); 6.71–8.15 (m, 15H, H-ar); Elemental analysis (%): $C_{51}H_{64}O_{10}$ (837.14), (calcd./found): C: 73.17/73.01; H: 7.71/7.63; $[\alpha]_D^{22} = +3.5$; c = 0.03 ($CHCl_3$)

6f ^{1}H-NMR: 0.82–0.99 (m, 9H, 3 × CH_3); 1.01–1.04 (d, 3H, $CH(CH_3)$); 1.24–1.51 (m, 22H, 11 × CH_2); 1.63–1.95 (m, 5H, OCH_2CH_2, $OCH_2CH(CH_3)$, $C(O)CH_2CH_2$); 2.80 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.82–4.07 (m, 6H, 3 × OCH_2); 4.53 (t, 2H, J = 4.7 Hz, $COOCH_2$); 6.73–8.22 (m, 19H, H-ar)

6g ^{1}H-NMR: 0.84–0.87 (m, 9H, 3 × CH_3); 1.27–1.29 (d, 3H, $CH(CH_3)$); 1.31–1.51 (m, 28H, 14 × CH_2); 1.62–1.85 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.86 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.89–4.03 (m, 4H, 2 × OCH_2); 4.42–4.53 (m, 3H, $OCH(CH_3)$, $COOCH_2$); 6.70–8.13 (m, 15H, H-ar); Elemental analysis (%): $C_{54}H_{70}O_{10}$(879.14), (cacld./found): C: 73.76/73.81; H: 8.03/7.93

6h ^{1}H-NMR: 0.81–0.87 (m, 9H, 3 × CH_3); 1.24–1.27 (d, 3H, $CH(CH_3)$); 1.31–1.50 (m, 28H, 14 × CH_2); 1.53–1.88 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.80 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.99–4.07 (m, 4H, 2 × OCH_2); 4.12–4.56 (m, 3H, $OCH(CH_3)$, $COOCH_2$); 6.71–8.24 (m, 19H, H-ar); $[\alpha]_D^{22} = +1.5$; c = 0.04 ($CHCl_3$)

6i ^{1}H-NMR: 0.82–0.88 (m, 6H, 2 × CH_3); 1.23–1.49 (m, 20H, 10 × CH_2); 1.72–1.83 (m, 4H, OCH_2CH_2, $C(O)CH_2CH_2$); 2.49 (t, 2H, J = 7.6 Hz, $C(O)CH_2$); 3.91–3.99 (m, 4H, 2 × OCH_2); 4.48 (t, 2H, J = 4.8 Hz, $COOCH_2$); 6.60–8.32 (m, 15H, H-ar); Elemental analysis (%): $C_{54}H_{47}NO_{11}$ (885.97), (calcd./found): C: 72.93/72.73; H: 6.89/6.89; N: 1.81/1.74

6k ^{1}H-NMR: 0.81–0.91 (m, 6H, 2 × CH_3); 1.22–1.49 (m, 20H, 10 × CH_2); 1.78–1.85 (m, 4H, OCH_2CH_2, $C(O)CH_2CH_2$); 2.45 (t, 2H, J = 7.5 Hz, $C(O)CH_2$); 3.94–4.07 (m, 4H, 2 × OCH_2); 4.50 (t, 2H, $COOCH_2$); 6.64–8.33 (m, 19H, H-ar)

7b ^{1}H-NMR: 0.81–0.91 (m, 9H, 3 × CH_3); 1.23–1.50 (m, 30H, 15 × CH_2); 1.76–1.81 (m, 6H, 2 × OCH_2CH_2, $C(O)CH_2CH_2$); 2.47 (t, 2H, $C(O)CH_2$); 3.92–4.07 (m, 6H, 3 × OCH_2); 4.48 (t, 2H, J = 4.8 Hz, $COOCH_2$); 6.62–8.28 (m, 19H, H-ar)

7c ^{1}H-NMR: 0.82–0.88 (m, 9H, 3 × CH_3); 1.24–1.49 (m, 30H, 15 × CH_2); 1.60–1.84 (m, 6H, 2 × OCH_2CH_2, $C(O)CH_2CH_2$); 2.48 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.98–4.06 (m, 6H, 3 × OCH_2); 4.49 (t, 2H, $COOCH_2$); 6.63–8.18 (m, 14H, H-ar); Elemental analysis (%): $C_{54}H_{69}ClO_{10}$ (913.59), (calcd./found): C: 71.02/71.11; H: 7.62/7.81; Cl: 3.83/4.04

7d Elemental analysis (%): $C_{61}H_{73}ClO_{12}$ (1033.70), (calcd./found): C: 70.90/71.07; H: 7.13/7.13; Cl: 3.39/3.28

7e ^{1}H-NMR: 0.85–0.96 (m, 9H, 3 × CH_3); 1.01–1.02 (d, 3H, $CH(CH_3)$); 1.23–1.53 (m, 22H, 11 × CH_2); 1.56–1.90 (m, 5H, OCH_2CH_2, $OCH_2CH(CH_3)$, $C(O)CH_2CH_2$); 2.86 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.81 (t, 2H, J = 4.2 Hz, OCH_2); 4.01–4.04 (m, 4H, 2 × OCH_2); 4.51 (t, 2H, J = 4.9 Hz, $COOCH_2$); 6.72–8.13 (m, 15H, H-ar); $[\alpha]_D^{22} = +2.3$; c = 0.1 ($CHCl_3$)

7f ^{1}H-NMR: 0.82–1.03 (m, 9H, 3 × CH_3); 1.25–1.27 (d, 3H, $CH(CH_3)$); 1.30–1.50 (m, 22H, 11 × CH_2); 1.63–1.91 (m, 5H, OCH_2CH_2, $OCH_2CH(CH_3)$, $C(O)CH_2CH_2$); 2.87 (t, 2H, J = 4.7 Hz, $C(O)CH_2$); 3.67–3.84 (m, 2H, OCH_2 $CH(CH_3)$); 4.00–4.07 (m, 4H, 2 × OCH_2); 4.52 (t, 2H, J = 4.7 HZ, $COOCH_2$); 6.71–8.28 (m, 19H, H-ar)

7g ^{1}H-NMR: 0.84–0.87 (m, 9H, 3 × CH_3); 1.25–1.27 (d, 3H, $CH(CH_3)$); 1.28–1.49 (m, 28H, 14 × CH_2); 1.65–1.87 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.86 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.99–4.06 (m, 4H, 2 × OCH_2); 4.35–4.44 (m, 1H, $OCH(CH_3)$), 4.49–4.54 (t, 2H, J = 4.8 Hz, $COOCH_2$); 6.74–8.13 (m, 15H, H-ar); Elemental analysis (%): $C_{54}H_{70}O_{10}$ (879.14), (calcd./ found): C: 73.76/73.89; H: 8.03/8.01; $[\alpha]_D^{22} = +1.5$; c = 0.05 ($CHCl_3$)

7h ^{1}H-NMR: 0.82–0.88 (m, 9H, 3 × CH_3); 1.24–1.28 (d, 3H, $CH(CH_3)$); 1.29–1.50 (m, 28H, 14 × CH_2); 1.62–1.88 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.49 (t, 2H, J = 7.6 Hz, $C(O)CH_2$); 3.96–4.07 (m, 4H, 2 × OCH_2); 4.37–4.52 (m, 3H, $OCH(CH_3)$), $COOCH_2$); 6.65–8.29 (m, 19H, H-ar); $[\alpha]_D^{22} = +2.0$; c = 0.01 ($CHCl_3$)

7i ^{1}H-NMR: 0.82–0.87 (m, 6H, 2 × CH_3); 1.25–1.49 (m, 20H, 10 × CH_2); 1.65–1.84 (m, 4H, OCH_2CH_2, $C(O)CH_2CH_2$); 2.88 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 4.03–4.09 (m, 4H, 2 × OCH_2); 4.53 (t, 2H, J = 4.5 Hz, $COOCH_2$); 6.73–8.26 (m, 15H, H-ar); Elemental analysis (%): $C_{47}H_{53}NO_9$ (775.94), (calcd./found): C: 72.74/72.93; H: 6.89/7.05; N: 1.81/1.76

7k Elemental analysis (%): $C_{54}H_{57}NO_{11}$ (896.05), (calcd./found): C: 72.37/72.26; H: 6.42/6.40; N: 1.56/146

7l ^{1}H-NMR: 0.84–0.89 (m, 9H, 3 × CH_3); 1.25–1.26 (d, 3H, $CH(CH_3)$); 1.27–1.49 (m, 28H, 14 × CH_2); 1.63–1.84 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.87 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 4.03–4.11 (m, 4H, 2 × OCH_2); 4.41–4.47 (m, 1H, $OCH(CH_3)$); 4.55 (t, 2H, J = 5.2 Hz, $COOCH_2$); 6.76–8.27 (m, 18H, H-ar)

7m ^{1}H-NMR: 084–0.89 (m, 9H, 3 × CH_3); 1.25–1.28 (d, 3H, $CH(CH_3)$); 1.31–1.49 (m, 28H, 14 × CH_2); 1.61–1.84 (m, 6H, $OCH_2CH_2CH_2$, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.87 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 4.02–4.16 (t, 4H, 2 × OCH_2); 4.51–4.57 (m, 3H, $OCH(CH_3)$, $COOCH_2$); 6.71–8.88 (m, 18H, H-ar)

Transition temperatures of the homologous series **8** in (°C):

no.	z	Cr	S_C^*	Ch	Is
8a	4	· 124	(· 105)	· 165	·
8b	5	· 122	· 124	· 157	·
8c	6	· 116	· 124	· 163	·
8d	7	· 119	· 133	· 159	·
8e	8	· 118	· 141	· 160	·
8f	9	· 106	· 142	· 159	·
8g	10	· 107	· 142	· 161	·

8e ^{1}H-NMR: 0.81–0.87 (m, 9H, 3 × CH_3); 1.24–1.27 (d, 3H, $CH(CH_3)$); 1.31–1.50 (m, 28H, 14 × CH_2); 1.53–1.88 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.79 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.99–4.07 (m, 4H, 2 × OCH_2); 4.12–4.56 (m, 3H, $OCH(CH_3)$, $COOCH_2$); 6.71–8.24 (m, 19H, H-ar); $[\alpha]_D^{22} = +1.5$; c = 0.04 ($CHCl_3$)

9a ^{1}H-NMR: 0.85–0.89 (m, 9H, 3 × CH_3); 1.25–1.48 (m, 30H, 15 × CH_2); 1.61–1.84 (m, 6H, 2 × OCH_2CH_2, $C(O)CH_2CH_2$); 2.73 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.98–4.05 (m, 6H, 3 × OCH_2); 4.53 (t, 2H, J = 4.8 Hz, $COOCH_2$); 6.67–8.16 (m, 19H, H-ar)

9b ^{1}H-NMR: 0.84–0.88 (m, 9H, 3 × CH_3); 1.31–1.34 (d, 3H, J = 6.0 Hz, $CH(CH_3)$); 1.28–1.50 (m, 28H, 14 × CH_2); 1.64–1.84 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.74 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.97–4.06 (m, 4H, 2 × OCH_2); 4.36–4.42 (m, 1H, $OCH(CH_3)$); 4.53 (t, 2H, J = 4.6 Hz, $COOCH_2$); 6.67–8.17 (m, 19H, H-ar)

9c ^{1}H-NMR: 0.82–0.87 (m, 9H, 3 × CH_3); 1.31–1.34 (d, 3H, J = 6.0 Hz, $CH(CH_3)$); 1.24–1.50 (m, 28H, 14 × CH_2); 1.60–1.94 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.43 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.94 (t, 2H, J = 4.9 Hz, OCH_2); 4.12 (t, 2H, J = 6.5 Hz, OCH_2); 4.36–4.45 (m, 1H, $OCH(CH_3)$); 4.49 (t, 2H, J = 4.8 Hz, $COOCH_2$); 6.60–8.20 (m, 18H, H-ar); $[\alpha]_D^{22} = -1.2$; c = 0.05 ($CHCl_3$)

9d ^{1}H-NMR: 0.85–0.88 (m, 9H, 3 × CH_3); 1.30–1.33 (d, 3H, $CH(CH_3)$); 1.34–1.53 (m, 28H, 14 × CH_2); 1.62–1.82 (m, 6H, OCH_2CH_2, $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.87 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.89–4.03 (m, 4H, 2 × OCH_2); 4.36–4.45 (m, 1H, $OCH(CH_3)$); 4.53 (t, 2H, J = 4.7 Hz, $COOCH_2$); 6.75–8.23 (m, 19H, H-ar)

9e ^{1}H-NMR: 0.83–0.87 (m, 9H, 3 × CH_3); 1.28–1.31 (d, 6H, 2 × $CH(CH_3)$); 1.34–1.51 (m, 26H, 13 × CH_2); 1.61–1.75 (m, 6H, 2 × $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.74 (t, 2H, J = 7.4 Hz, $C(O)CH_2$); 3.99 (t, 2H, J = 4.6 Hz, OCH_2); 4.36–4.51 (m, 2H, 2 × $OCH(CH_3)$); 4.53 (t, 2H, $COOCH_2$); 6.67–8.17 (m, 19H, H-ar); $[\alpha]_D^{22} = -0.8$; c = 0.05 ($CHCl_3$)

9f ^{1}H-NMR: 0.84–0.89 (m, 9H, 3 × CH_3); 1.24–1.27 (d, 6H, 2 × $CH(CH_3)$); 1.28–1.48 (m, 26H, 13 × CH_2); 1.60–1.79 (m, 6H, 2 × $OCH(CH_3)CH_2$, $C(O)CH_2CH_2$); 2.75 (t, 2H, J = 7.5 Hz, $C(O)CH_2$); 4.02 (t, 2H, J = 4.8 Hz, OCH_2); 4.39–4.42 (m, 2H, 2 × $OCH(CH_3)$); 4.54 (t, 2H, J = 4.8 Hz, $COOCH_2$); 6.69–8.23 (m, 23H, H-ar)

10a Elemental analysis (%): $C_{52}H_{66}O_{11}$ (867.02), (calcd./found): C: 71.77/71.56; H: 7.15/7.04

10b ^{1}H-NMR: 0.88–0.92 (m, 9H, 3 × CH_3); 1.30–1.31 (d, 3H, $CH(CH_3)$); 1.32–1.50 (m, 24H, 12 × CH_2); 1.54–1.83 (m, 6H, OCH_2CH_2, $COOCH_2CH_2$, $OCH(CH_3)CH_2$); 3.62 (t, 2H, $COOCH_2$); 4.04 (t, 2H, OCH_2); 4.24 (t, 2H, OCH_2); 4.39–4.42 (m, 1H, $OCH(CH_3)$); 4.54 (t, 2H, $COOCH_2$); 6.71–8.27 (m, 23H, H-ar)

11a ^{1}H-NMR: 0.84–0.88 (m, 6H, 2 × CH_3); 1.11–1.12 (d, 3H, $CH(CH_3)$); 1.27 (s, 9H, $C(CH_3)_3$); 1.30–1.46 (m, 18H, 9 × CH_2); 1.60–1.84 (m, 4H,

OCH_2CH_2, $OCH(CH_3)CH_2$); 3.97–4.07 (m, 4H, 2 × OCH_2); 4.47–4.52 (m, 3H, $OCH(CH_3)$, $COOCH_2$); 6.68–8.29 (m, 19H, H-ar); Elemental analysis (%): $C_{49}H_{62}O_9$ (759.03), (calcd./found): C: 73.52/73.47; H: 7.22/7.20; $[\alpha]_D^{22} = +1.2$; c = 0.05 ($CHCl_3$)

11b ^{1}H-NMR: 0.85–0.92 (m, 6H, 2 × CH_3); 1.18–1.19 (d, 3H, $CH(CH_3)$); 1.21 (s, 9H, $C(CH_3)_3$); 1.22–1.52 (m, 18H, 9 × CH_2); 1.59–1.85 (m, 4H, OCH_2CH_2, $OCH(CH_3)CH_2$); 3.91–4.07 (m, 4H, 2 × OCH_2); 4.36–4.52 (m, 3H, $OCH(CH_3)$, $COOCH_2$); 6.60–8.29 (m, 23H, H-ar)

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