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Stabilization of the S_C Phase in Mixtures of Laterally Aryl Substituted Mesogens

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Laterally 4-nitrobenzyloxycarbonyl substituted three-ring compounds preferably exhibit smectic A phases. However, induction of smectic C phases can be observed in binary mixtures with mesogens having a similar molecular shape but not a strongly polar group at the laterally positioned phenyl ring. The scale of phase induction depends on the length of terminal alkyl chains, type and position of substituents as well as the length of the flexible spacer linking the lateral aryl group to the basic mesogen. X-ray investigations of selected mixtures verify that the structure of induced smectic C phases is intercalated comparable to orthogonal phases of lateral aryl substituted mesogens.

Keywords: Laterally branched liquid crystals; induced smectic C phases; binary mixtures; X-ray

1. INTRODUCTION

In binary systems the intermolecular interaction can be systematically changed by the concentration of the components. In this way a stabilization [1–3] or a destabilization [3–5] of liquid crystalline phases can occur. Stabilization of smectic phases with respect to nematic or isotropic phases can be due to dipole–dipole interactions [2], EDA complexing [6–8] or/and steric factors [9–11].

The stabilization of a liquid crystalline phase in a mixture is generally designated as “phase induction”. Phase induction was observed in mixtures of low-molecular mesogens as well as in binary systems with main-chain or side-group liquid-crystalline polymeric components [12–14]. Recently,

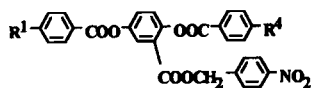
* Corresponding author.

induced phases in binary systems of nematic twin compounds were described. In dependence on the even or odd numbered spacer length induced smectic A or smectic C phases are formed [15]. In most cases smectic A phases, sometimes smectic B or E phases are induced. To our knowledge there are only few examples for the induction of a smectic C phase [15–18]. The stabilization of smectic C phases in binary mixtures is also of practical relevance because smectic C phases with a wide temperature range can be used as matrix for ferroelectric S_C^* mixtures.

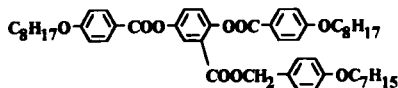
Mesogens having a substituted aromatic ring in the lateral segment are characterized by a wedge-like molecular shape and exhibit unexpectedly high clearing points. Generally, nematic and smectic A phases are preferentially observed for laterally aryl substituted compounds having a three-ring basic mesogen. According to results, recently reported, weakly electron-withdrawing properties of the substituents attached at the lateral phenyl ring can stimulate the formation of smectic C phases, but strong electron-accepting groups, like cyano or nitro, mainly favour the existence of S_A phases [19]. The molecules have an antiparallel packing in smectic layers which possess an intercalated structure [4, 18]. Mixtures of laterally aryl substituted compounds with rod-like and terminally branched mesogens and their calorimetric and dielectric behaviour have been already investigated [3, 20]. In this paper we want to report that in binary mixtures of two laterally aryl substituted compounds smectic C phases can be stabilized in a wide concentration range depending on the chemical constitution of the single compounds. In the most examples (series I–III) one of the mixing components (B) is unchanged. Number and type of substituents of the second component (A) are varied. In all derivatives A1–A33 a strongly electron-accepting nitro or cyano group, respectively, is attached at the lateral phenyl ring. In the series I the length of one or both of the terminal alkyloxy chains R^1 and R^4 component A will be changed. In the series II the variation is done in the rod-like basic molecule of component A bearing a lateral 4-nitrobenzyloxycarbonyl group. Additional chloro atoms are introduced in R^2 or/and R^3 and the electronical properties of the substituents R^1 or R^4 is changed by using cyano or alkylamino groups. In the series III the lateral segment linked to *p*-phenylene *bis* (4-*n*-octyloxybenzoate) is varied by lengthening the spacer X as well as the position and type of the substituents R^5 – R^7 attached to the lateral phenyl ring. Finally, component A is unchanged in series IV, herein the lateral segment of component B is varied concerning the spacer as well as the substituents in *para*-position of the lateral phenyl ring.

First, the mesogenic behaviour of the pure mixing components is described. Then, the isobaric phase diagrams of some selected binary

Series I

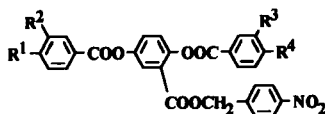


A1-A14

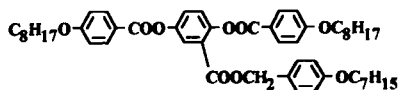


B1

Series II

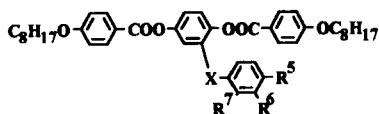


A15-A26

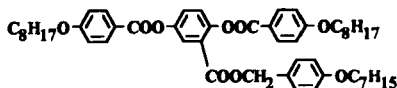


B1

Series III

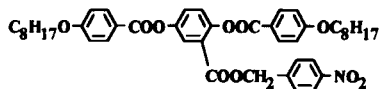


A27-A33

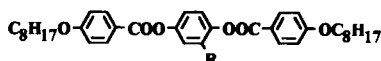


B1

Series IV



A3



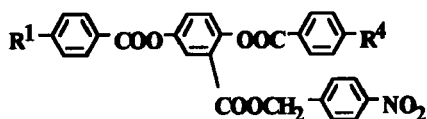
B1-B6

mixtures are presented where the structure of the compounds are systematically varied. The influence of the different molecular segments on the induction of smectic C phases will be discussed. For one representative binary system the results of X-ray investigations are presented.

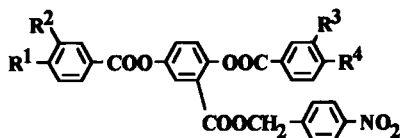
2. MATERIALS

The compounds used for the investigations are listed in the Tables I–IV classified according to the point of view of the mixing series I–IV. Some of the derivatives have been already published. The other ones were prepared according to the methods described [21]. Therefore, only the general reaction path should be discussed herein. To synthesize the compounds

TABLE I Mesophase behaviour of the compounds A1–A14

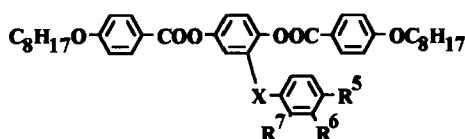


No.	R^1	R^4	Cr	S_A	N	Is
A1 [20]	C_4H_9O	OC_4H_9	·134	(·108)	·155	·
A2 [20]	$C_6H_{13}O$	OC_6H_{13}	·110	·151	·154	·
A3 [20]	$C_8H_{17}O$	OC_8H_{17}	·96	·163	—	·
A4 [20]	$C_{10}H_{21}O$	$OC_{10}H_{21}$	·87	·168	—	·
A5 [3]	$C_{14}H_{29}O$	$OC_{14}H_{29}$	·92	·167	—	·
A6	$C_8H_{17}O$	OCH_3	·138	—	(·134)	·
A7	$C_8H_{17}O$	OC_2H_5	·133	(·98)	·140	·
A8	$C_8H_{17}O$	OC_3H_7	·132	(·123)	·141	·
A9	$C_8H_{17}O$	OC_4H_9	·129	·140	·147	·
A10	$C_8H_{17}O$	OC_5H_{11}	·121	·149	—	·
A11	$C_8H_{17}O$	OC_6H_{13}	·116	·155	—	·
A12	$C_8H_{17}O$	OC_7H_{15}	·97	·158	—	·
A13	$C_8H_{17}O$	OC_9H_{19}	·97	·164	—	·
A14	$C_8H_{17}O$	$OC_{10}H_{21}$	·98	·165	—	·

TABLE II Influence of different substituents R^1 – R^4 on the mesophase behaviour of 2,5-disubstituted 4-nitrobenzyl benzoates

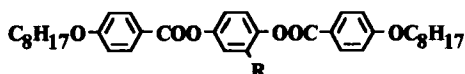
No.	R^1	R^2	R^3	R^4	Cr	S_C	S_A	N	Is
A3 [20]	$C_8H_{17}O$	H	H	OC_8H_{17}	·96	—	·163	—	·
A15	$C_8H_{17}O$	H	H	$OC_8^*H_{17}$	·90	—	·113	—	·
A16 [21]	$C_8H_{17}O$	Cl	H	OC_8H_{17}	·90	—	·155	—	·
A17 [21]	$C_8H_{17}O$	H	Cl	OC_8H_{17}	·83	—	·150	—	·
A18 [21]	$C_8H_{17}O$	Cl	Cl	OC_8H_{17}	·120	—	·139	—	·
A19	$C_8H_{17}O$	H	H	CN	·148	—	—	(·132)	·
A20	NC	H	H	OC_8H_{17}	·198 ¹	—	—	—	·
A21	$C_8H_{17}O$	H	H	$N(CH_3)C_8H_{17}$	·100	(·68	—	·84)	·
A22	$C_8H_{17}(CH_3)N$	H	H	OC_8H_{17}	·94	(·72	—	·89)	·
A23	$C_8H_{17}(CH_3)N$	H	H	$N(CH_3)C_8H_{17}$	·83 ²	—	—	—	·
A24	$C_8H_{17}(CH_3)N$	H	H	$OC_8^*H_{17}$	·87 ²	—	—	—	·
A25	$C_8H_{17}O$	H	H	NHC_8H_{17}	·151	—	—	(·150)	·
A26	C_8H_{17}	H	H	C_8H_{17}	·102	—	·135	—	·

¹ recrystallization at 197°C.² no mesophase on cooling upto 20°C.

TABLE III Influence of the spacer X and the substituents R⁵–R⁷ attached at the lateral phenyl on the mesophase behaviour

No.	X	R ⁵	R ⁶	R ⁷	Cr	S _A	N	Is
A27	COOCH ₂	CN	H	H	.91	.152	–	.
A28	COOCH ₂	H	CN	H	.82	.82	.103	.
A29	COOCH ₂	H	H	CN	.95	–	(.90)	.
A30	COOCH ₂	H	H	NO ₂	.108	–	(.80)	.
A31	COOCH ₂ CH ₂ O	NO ₂	H	H	.90	.174	–	.
A32	COOCH ₂ CH ₂ O	H	NO ₂	H	.117	(.106)	.114	.
A33 [20]	COO(CH ₂) ₈ O	NO ₂	H	H	.52	.72	.100	.

TABLE IV Variation of the bulky lateral substituent R of the components B



No.	R	Cr	S _C	S _A	N/N*	Is
B1 [22]	COOCH ₂ –C ₆ H ₄ –OC ₇ H ₁₅	.70	(.61)	–	.105	.
B2 [22]	COOCH ₂ –C ₆ H ₄ –OC ₂ H ₅	.92	–	–	.117	.
B3	COO(CH ₂) ₂ O–C ₆ H ₄ –OC ₈ H ₁₇	.128	–	–	(.119)	.
B4 [23]	COO(CH ₂) ₂ O–C ₆ H ₄ –COOC ₂ H ₁₁	.84	.91	–	.111	.
B5 [24]	COO(CH ₂) ₂ O–C ₆ H ₄ –COC ₂ H ₅	.105	.123	.133	.145	.
B6 [24]	COO(CH ₂) ₂ O–C ₆ H ₄ –C(CH ₃) ₃	.90	(.61)	–	.91	.

A1–A5, A18, A23, A26–A33 having identical substituents at both terminal positions of the basic mesogens (R¹ = R⁴; R² = R³) the appropriate 2,5-dihydroxybenzoic esters can be acylated with the substituted benzoic acids or benzoyl chlorides, respectively. Nonsymmetrical 2,5-disubstituted gentisic acid derivatives A6–A17, A19–A22, A24, A25 were prepared by regioselective esterification of appropriate 2,5-dihydroxybenzoic esters in 5-position with a substituted benzoic acid by means of dicyclohexylcarbodiimide and following acylation in 2-position with a suitable benzoyl chloride. Mesogens B1–B6 can be synthesized by reaction of 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoylchloride with 4-substituted benzylic alcohols or phenoxyethanols or by esterification of the gentisic acid esters already bearing the whole lateral group with 4-*n*-octyloxybenzoyl chloride. Chemical

constitution and purity of all the compounds under discussion were estimated by elemental analysis and NMR-spectroscopic investigations.

The nonsymmetrical substituted dialkyloxy derivatives **A6–A14** exhibit a phase behaviour comparable to that of the symmetric compounds [20]. Nematic phase exists for the short-chained mesogens, only. The stability of the smectic A phase increases with increasing length of the terminal groups as shown in Figure 1 for the homologous series **A6–A14** + **A3**. The liquid crystalline behaviour of laterally aryl substituted mesogens changed by different groups at the positions R^1 – R^4 is summarized in Table II. Substitution of R^2 or/and R^3 in the basic mesogen by chloro yielding **A16–A18** do not depress the smectic A–isotropic transition temperatures markedly. However, in spite of the voluminous lateral segment existing in the mesogens the clearing points are strongly decreased by branching of one terminal chain with a methyl group (**A15**, **A21**, **A22**). Branches in both terminal wing groups prevent the existence of mesophases (**A23**, **A24**). One cyano group attached at the basic mesogen causes an striking increase of the melting points (**A19**, **A20**).

If the cyano or nitro group is linked at the *meta*- or *ortho*-position of the lateral phenyl ring (R^6 or R^7) the clearing points are decreased and nematic phases appear, as summarized in Table III. The existence range of smectic phases are reduced or disappear. The same tendency is observed if the spacer X is too long and flexible, see compound **A33**.

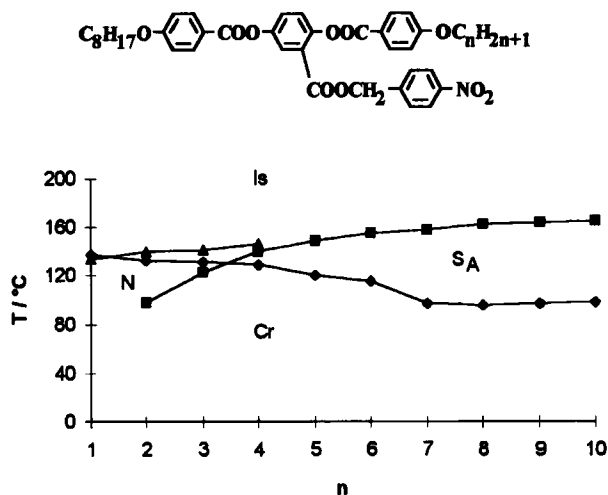


FIGURE 1 Phase transitions of the homologous series **A3**, **A6–A14**.

The liquid crystalline behaviour of the mixing compounds **B** without strongly polar cyano or nitro group at the lateral phenyl ring is given in Table IV. In comparison with the mesogens having a nitro group in R⁵ the clearing points are depressed. Some compounds show smectic C phases, the existence range of the smectic A phase is reduced or missed. Electron-accepting substituents in *para*-position of the phenyl ring of the lateral branch support the formation of layer structures.

3. BINARY SYSTEMS

The mesophase behaviour of the pure compounds as well as of the mixing systems was observed by means of polarizing microscopy. The phase diagrams of binary systems (Figs. 2–5) were constructed by determination of the transition temperatures of selected mixtures having known concentrations.

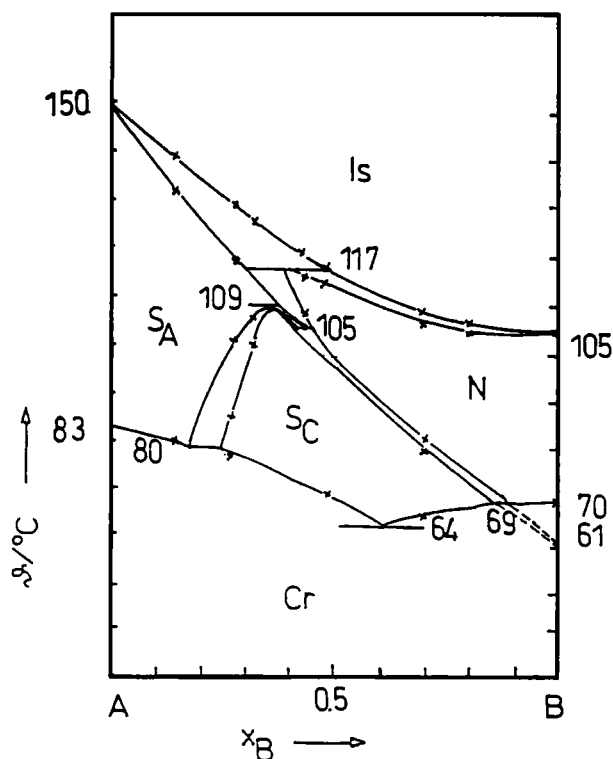


FIGURE 2 Phase diagram of binary mixture A17/B1 (See Tab. VI).

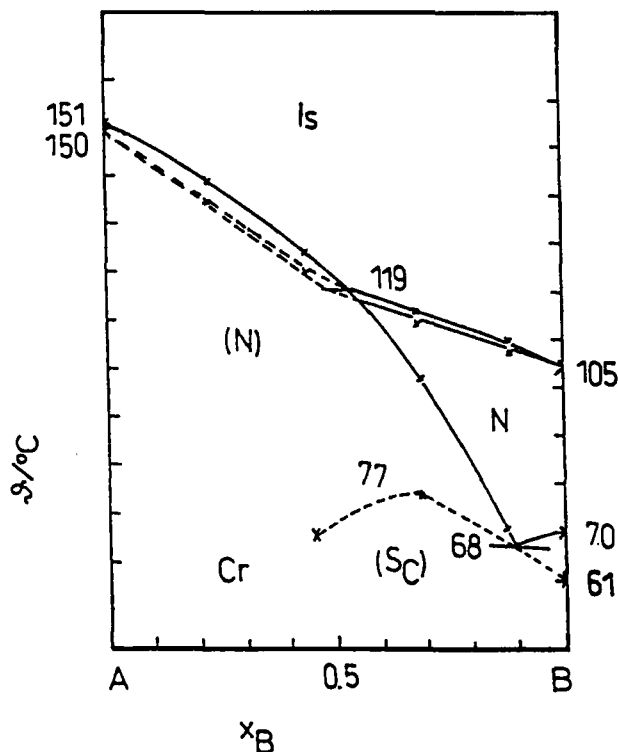


FIGURE 3 Phase diagram of binary mixture **A25/B1** (See Tab. VI).

In the other cases observations of contact preparations were done. In the following part the influence of the different molecular segments on the smectic C phase induction is discussed. The degree of phase stabilization in relationship to the number, type and position of substituents is investigated and discussed in the series I–IV.

Series I: Variation of the Terminal Alkyloxy Chains in R¹ and R⁴ of the Polar Component A

In series I compound **B1** (Cr 70 (S_C 61) N 105 Is) was combined with some homologues of the 4-nitrobenzyl esters **A1**–**A14** characterized by different length of the alkyloxy chains in R¹ and R⁴. None of the components A exhibits a tilted phase structure. The induction of the S_C phase in the binary systems studied is expressed by the temperature difference $\Delta T_{SC} = T_{max} - T_{B1}$ where T_{B1} is the transition temperature S_C–N of the

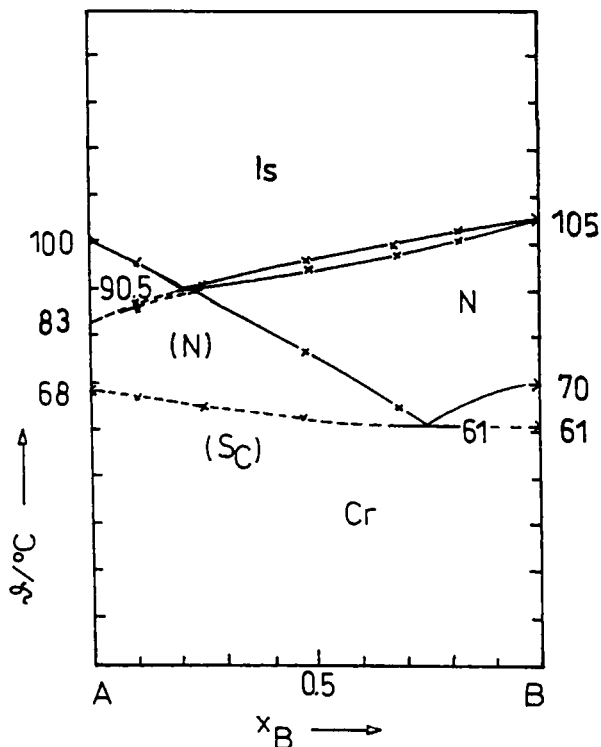


FIGURE 4 Phase diagram of binary mixture A21/B1 (See Tab. VI).

compound **B1** and T_{\max} is the maximum temperature of the S_C mixed phase region.

As seen Table V ΔT_{SC} depends on the length of the terminal aliphatic chains. Maximum induction can be observed when the number of carbon atoms in both chains together is about 16 or more. The greatest value found for ΔT_{SC} is 54 K. Both alkyloxy chains R¹, R⁴ can have the same length or can also differ.

Series II: Influence of the Substituents R¹–R⁴ Linked at the Basic Mesogen of the Components A

The results given in Table VI demonstrate the strong influence of different substituents attached at the basic mesogen on the degree of S_C phase stabilization. Contact preparations which do not exhibit smectic C phase induction are indicated by a minus symbol for ΔT_{SC} . Mixing behaviour shown in Figures 2–5 resulting from investigations with single concentra-

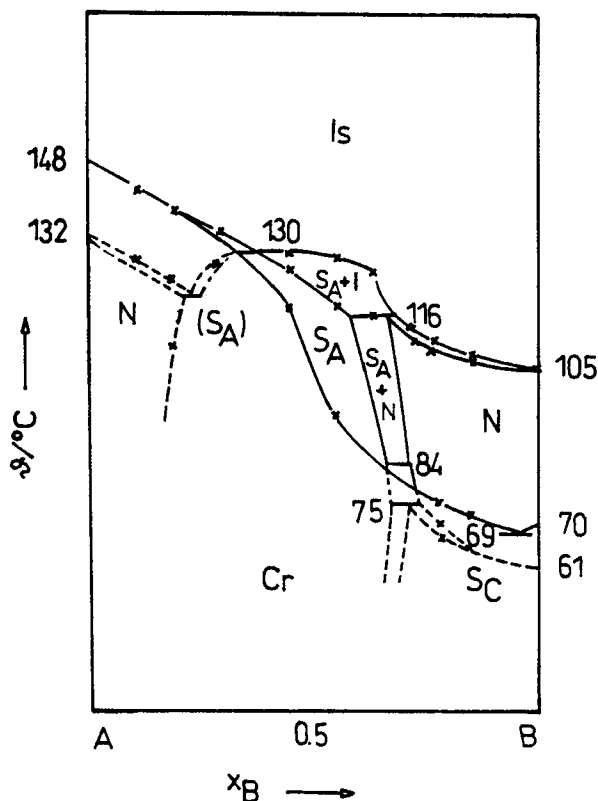
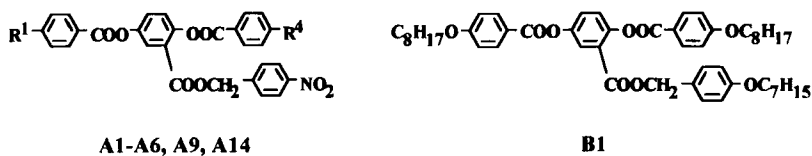


FIGURE 5 Phase diagram of binary mixture **A19/B1** (See Tab. VI).

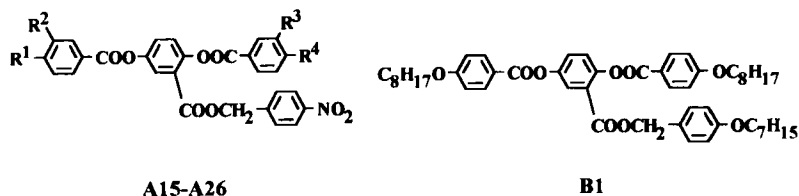
tions are suitable to demonstrate various types of phase diagrams. The introduction of additional chloro atoms into the basic mesogen yielding compounds **A16–A18** does not markedly change the scale of phase induction in appropriate mixtures with substance **B1**. As seen in Figure 2, the S_C phase exists in the binary system **A17/B1** in a wide concentration range between 0.2–1 mole fraction B. This phase diagram is considered to be typical for systems under discussion where a S_C phase is stabilized, *e.g.*, in series I, too. As shown in Figure 3 the exchange of one octyloxy chain (**A3**) by an octylamino group (**A25**) having the same chain length in R⁴ yields a monotropic S_C phase resulting from a smaller effect of phase induction of $\Delta T_{SC} = 16$ K. Substitution of the terminal octylamino group in the derivative **A25** by the branched *N*-methyl-*N*-octylamino group in compound **A21** results in the loss of phase induction, as shown in Figure 4. Both components of the binary system **A21/B1** possess a S_C phase. Complete miscibility

TABLE V Induction of smectic C phases in mixtures of compound **B1** with components A in dependence on the chain length of the alkyloxy groups R¹ and R⁴

No.	R ¹	R ⁴	ΔT _{SC} [K] ^(a)
A1	C ₄ H ₉ O	OC ₄ H ₉	(b)
A2	C ₆ H ₁₃ O	OC ₆ H ₁₃	42
A3	C ₈ H ₁₇ O	OC ₈ H ₁₇	54
A4	C ₁₀ H ₂₁ O	OC ₁₀ H ₂₁	52
A5	C ₁₄ H ₂₉ O	OC ₁₄ H ₂₉	51
A6	C ₈ H ₁₇ O	OCH ₃	(b)
A9	C ₈ H ₁₇ O	OC ₄ H ₉	30
A14	C ₈ H ₁₇ O	OC ₁₀ H ₂₁	53

^(a) ΔT_{SC} = T_{max} - T_{B1} (T_{max}: temperature of the maximum of the smectic C mixed phase region, T_{B1}: transition temperature S_C/N of the compound **B1**).

^(b) rapid crystallization.

TABLE VI Mixing behaviour of compound **B1** with components A varied at the substituents R¹ - R⁴

No. comp. A	R ¹	R ²	R ³	R ⁴	ΔT _{SC} [K]
A15	C ₈ H ₁₇ O	H	H	OC ₈ H ₁₇	—
A16	C ₈ H ₁₇ O	Cl	H	OC ₈ H ₁₇	46
A17	C ₈ H ₁₇ O	H	Cl	OC ₈ H ₁₇	48
A18	C ₈ H ₁₇ O	Cl	Cl	OC ₈ H ₁₇	44
A19	C ₈ H ₁₇ O	H	H	CN	— ¹
A20	NC	H	H	OC ₈ H ₁₇	— ²
A21	C ₈ H ₁₇ O	H	H	N(CH ₃)C ₈ H ₁₇	—
A22	C ₈ H ₁₇ (CH ₃)N	H	H	OC ₈ H ₁₇	—
A24	C ₈ H ₁₇ (CH ₃)N	H	H	OC ₈ H ₁₇	—
A25	C ₈ H ₁₇ O	H	H	NHC ₈ H ₁₇	16
A26	C ₈ H ₁₇	H	H	C ₈ H ₁₇	25

¹ stabilization of a S_A phase as seen in Figure 5.

² rapid crystallization.

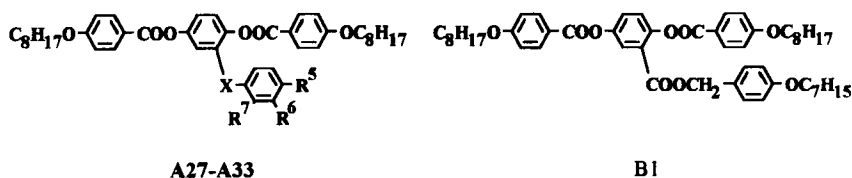
is found, but without phase induction. It can be seen from Figure 5 that the introduction of a cyano group in R^4 favours a strong induction of a smectic A phase at middle concentration ranges in the mixture A19/B1.

Series III: Variation of the Spacer X and of the Substituents R^5 – R^7 Linked to the Lateral Phenyl Ring

In the series I and II the components A are characterized by a lateral 4-nitrobenzyl ester group. Now, it is of interest to investigate how the induction of S_C phases depends on the position (R^5 – R^7) of the strongly polar substituent at the lateral aromatic ring of components A. Furthermore, the length of the spacer X connecting the lateral aryl group to the basic mesogen changes the flexibility between these two segments. The results are summarized in Table VII.

To observe a smectic C phase induction the cyano or nitro group has to be situated in *para*-position of the lateral phenyl ring. In the other mixtures of B1 and one component A (A28–30, A32) with the polar substituent in *meta* or *ortho* position (R^6 or R^7) no phase induction could be observed. By considerable lengthening the spacer X not only the existence of smectic phases of the pure compound A33 is reduced but also the ability to induce a smectic C phase.

TABLE VII Variation of the spacer and of the substituents R^5 – R^7 at the lateral attached phenyl ring of component A



No.	X	R^5	R^6	R^7	$\Delta T_{SC}[K]$
A27	COOCH ₂	CN	H	H	44
A28	COOCH ₂	H	CN	H	–
A29	COOCH ₂	H	H	CN	–
A30	COOCH ₂	H	H	NO ₂	–
A31	COOCH ₂ CH ₂ O	NO ₂	H	H	44
A32	COOCH ₂ CH ₂ O	H	NO ₂	H	–
A33	COO(CH ₂) ₈ O	NO ₂	H	H	– ¹

¹ stabilization of the S_A phase.

Series IV: Variation of the Bulky Lateral Substituent R of Component B

In a further of mixing investigations we used component **A3** whereas compound **B** bearing a low-polar bulky lateral segment is changed. The results are summarized in Table VIII.

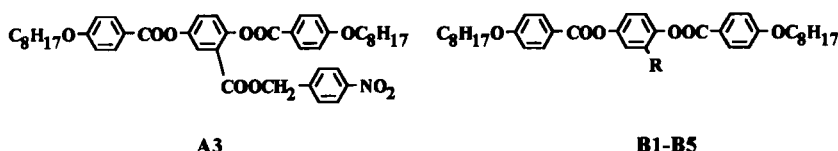
In all mixtures **A3/B1–B5** we found a stabilization of the S_C phase. But the results cannot directly compared with those given in the Tables V–VII because not all of the compounds **B** exhibit a S_C phase themselves. ΔT_{SC} cannot be determined in all cases. Therefore, the maximum temperatures T_{max} of the induced S_C mixed phase region are listed in the Table VIII.

4. X-RAY INVESTIGATIONS

X-ray investigations were performed in the region of the S_C phase (between 27–70 mole% of component A) for the binary system **A17/B1** presented in Figure 2. In Figure 6 the d -values of the S_C phases were plotted as function of the concentration. For comparison, the layer spacing d_A of the S_A phase of compound **A17** is drawn (3.25 nm). This value is essentially smaller than the molecular length L of compound **A** in its most stretched conformation (4.04 nm). The difference $L-d = 0.7$ nm can be interpreted by a structure model with a partial intercalation of the terminal alkyl chains [20]. To calculate the tilt angle β of the mixed phase we used the relation.

$$\cos \beta = \frac{d(S_C)}{d(S_A)} \quad \begin{array}{l} d(S_C) : d - \text{value of the } S_C \text{ phase} \\ d(S_A) : d - \text{value of the } S_A \text{ phase} \end{array}$$

TABLE VIII S_C phase induction in binary mixtures considering the variation of the bulky lateral segment of the components **B**



No.	R	T_{max} [°C]
B1	COOCH ₂ —C ₆ H ₄ —OC ₇ H ₁₅	115 ($\Delta T_{SC} = 54$ K)
B2	COOCH ₂ —C ₆ H ₄ —OC ₂ H ₅	97
B3	COO(CH ₂) ₂ O—C ₆ H ₄ —OC ₈ H ₁₇	123
B4	COO(CH ₂) ₂ O—C ₆ H ₄ —COOC [*] ₅ H ₁₁	118 ($\Delta T_{SC} = 27$ K)
B5	COO(CH ₂) ₂ O—C ₆ H ₄ —COC ₂ H ₅	123

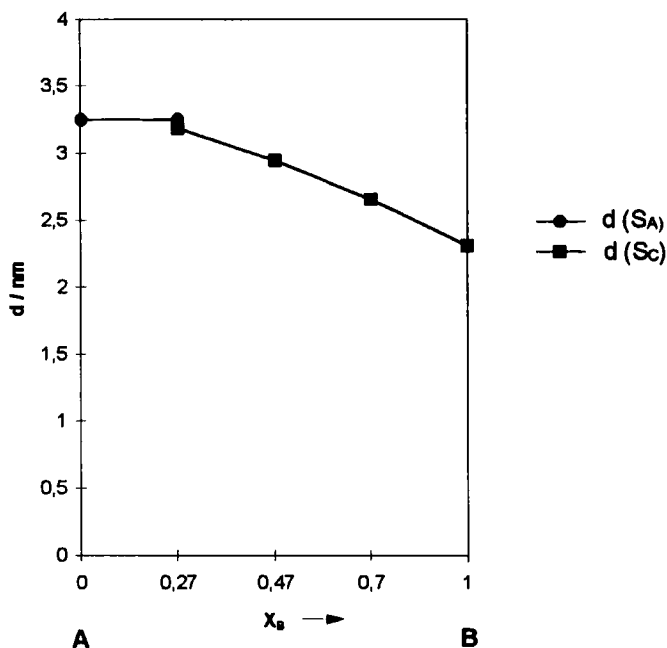


FIGURE 6 Layer spacing $d(S_A)$ and $d(S_C)$ in dependence on the molar fraction x_B for the binary system **A17/B1** (see Fig. 2).

For the mixture with $x_B = 0.27$ we obtained $d(S_A) = 3.25$ nm and $d(S_C) = 3.18$ nm (at $T = 60^\circ\text{C}$) and $\beta = 12^\circ$. The value $d(S_A)$ of the mixture is the same as that of the pure compound **A17**. This is understandable because the molecular length of the mixed compounds are equal. Applying the fact that this $d(S_A)$ value ($d(S_A) = 3.25$ nm) can be used for the following concentration, too (it means that the conformation of the molecule is independent of the concentration) the tilt can be calculated. The following values have been obtained: $x_B = 0.47$; $\beta = 25^\circ$; $x_B = 0.7$; $\beta = 35^\circ$; $x_B = 1.0$; $\beta = 45^\circ$. It should be emphasized that the d -values in the S_C phase are nearly independent of the temperature. The change of the tilt angle in dependence on the concentration is essential. The tilt angle tends to zero at the S_C/S_A transition. Further, the results point out that the intercalated structure which is assumed for the pure compounds is maintained in the mixture, too.

5. CONCLUSIONS

Laterally 4-nitrobenzyloxycarbonyl substituted three-ring mesogens (components **A1**–**A26**) prefer to exhibit S_A phases, however, in binary systems

under investigation S_C phases could be induced. Two conditions concerning the constitution of the components A must be satisfied. Firstly, a strongly polar substituent has to be present and secondly, this substituent has to be situated in *para* position at the laterally attached phenyl ring. The spacer X connecting this substituted aryl group with the basic mesogen should not be too long and too flexible. The occurrence of induced S_C phases in binary mixtures with components B having a similar molecular shape but not a strongly polar group at the lateral aromatic ring seems to be mainly because of dipole-induced dipole interactions. In mixtures of components A each other or components B each other (*e.g.*, **B1/B6**) no phase induction could be observed. X-ray investigations of selected mixtures show that the structure of the induced tilted C phase is intercalated analogous to smectic A phases of laterally aryl substituted mesogens.

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