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From laterally branched mesogens to novel twin molecules

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From laterally branched mesogens to novel twin molecules

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Extending a design concept for liquid-crystalline compounds with large lateral substituents, we have synthesized several new variants of twin compounds: lateral–terminal flexible bound, and lateral–lateral flexible bound with and without ring systems in the flexible spacer. X-ray investigations of the nematic phases of several new compounds proved the occurrence of reflections that are incompatible with the simple molecular dimensions. Models in which the two halves and ring-containing spacers of the twins are nearly parallel to one another can explain the experimental facts, assuming an interdigitation of the molecules in the nematic state. Several new compounds form nematic glass phases at about room temperature.

1. Introduction

The investigation of the relationship between molecular structure and properties in liquid-crystalline twin compounds is of real interest. The twins may be considered as prepolymers which are well suited for theoretical modelling. In addition to the chemical structure and the geometrical shape of the mesogenic units, the nature of their linking has a marked influence on the mesogenic behaviour. Scheme 1 displays some of the variants of how the two mesogenic units may be linked.

In the twins of type A the two mesogens are linked terminally by a flexible spacer. Twins of this kind have been known for a long time, thus 65 years ago Vorländer [1] reported the strong alternation of the clearing temperatures with the length of the spacer in such structures. Now numerous publications about twins of this type are known [2–7] because they are interesting as model compounds for main chain polymers. There are also conformational analyses by means of deuterium N.M.R. spectroscopy in compounds with deuteriated spacers [8, 9].

Malthete and co-workers [10, 11] synthesized twins of type B by four-fold acylation of 1,4,5,8-tetrahydroxy-naphthalene or -anthraquinone with appropriately substituted benzoyl chlorides. The authors first created the designation Siamese twin which was applied by Griffin *et al.* [12, 13] to structures of type C. Here both the mesogenic units are linked by a methylene group; that is, by a relatively rigid segment.

Numerous investigations concerning the conformation indicate that the molecules exist in the most extended form as sketched in scheme 1. Dehne *et al.* [14] recently described twins of type C which are ligated by thio, sulphinyl and sulphonyl bridges. The mesogenity increases with the oxidation number of sulphur in these compounds.

2. Results and discussion

2.1. *Phase behaviour*

In the twins of types A–C both mesogenic units in the most cases are identical (an exception are the very recently published unsymmetrically substituted hexanes [7]);

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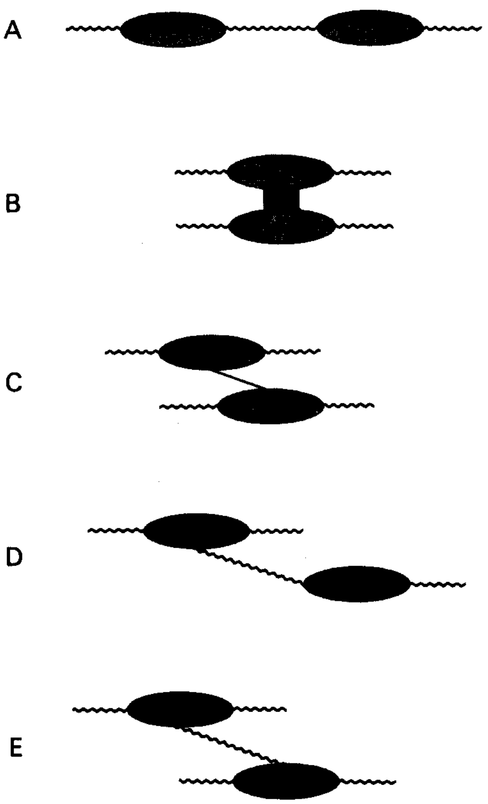
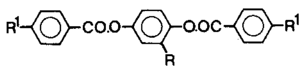
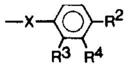


Scheme 1. Some variants of linking two mesogenic groups in twin molecules.

however, our novel variant D allows the convenient synthesis of non-symmetrically constructed twins. The results reported here are derived from our systematic investigation of the structure–properties relationships in liquid-crystalline compounds with long chain terminal and lateral substituents [15].

The nematic properties of the laterally alkyl substituted compounds **I** and the former unknown trend of the clearing temperatures in the homologous series with increasing lateral chain length could be explained by assuming that the lateral substituents are oriented approximately parallel to the molecular long axis. In addition compounds with bulkier lateral substituents, e.g. *t*-butyl **II** [16] or di-alkyl ketoxim esters **III** [17], may be mesogenic.

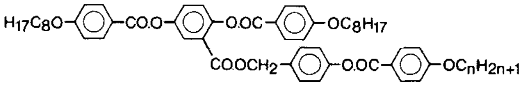


	R	
I	$-C_nH_{2n+1}$	[15]
II	-*t*-butyl	[16]
III	$-COO-N=C\begin{matrix}C_nH_{2n+1}\\ C_nH_{2n+1}\end{matrix}$	[17]
IV		[18]

Recently we described the new liquid crystals **IV** in which cyclic moieties (aromatic, cycloaliphatic or heterocyclic rings) are laterally bound by a flexible spacer to three-ring compounds [18]. These substances exhibit unexpectedly high clearing temperatures, especially if the aliphatic spacer is odd numbered with at least three segments. In these cases the cyclic moiety itself may be substituted in a different manner. In the 4 position of the lateral phenyl ring, *n*-alkyl, *n*-acyl and *n*-alkyloxy groups as well as small polar groups (halogen, nitro and cyano) increase the clearing temperatures. By further development of this concept we have synthesized the non-symmetrical twin molecules of type D. These are characterized by the terminal binding of a mesogenic two- or three-ring systems by means of an odd spacer at the middle ring of a three-ring compound. Thus a lateral–terminal binding of the two mesogens according to type D results.

Table 1 presents the compounds **1–7** in which the lateral mesogens are phenyl 4-*n*-alkyloxybenzoates coupled by a methylenoxycarbonyl spacer with the phenylene-1,4-bis-(4-*n*-octyloxybenzoate). In this series, below the enantiotropic nematic phases additional monotropic smectic C phases exist. Surprisingly the clearing temperatures are nearly independent on the length of the alkyloxy chain.

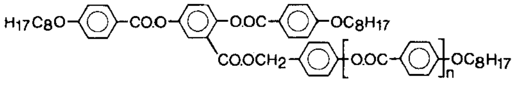
Table 1. 4-(4-*n*-Alkyloxybenzoyloxy)-benzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)-benzoates; transition temperatures are in °C.



No.	*n*	C	S_C	N	I
1	4	● 121	–	● 152·5	●
2	5	● 120	(● 58·5)	● 153	●
3	6	● 110	(● 77·5)	● 153·5	●
4	7	● 108	(● 83)	● 152	●
5	8	● 99	(● 88·5)	● 151·5	●
6	9	● 99	(● 93)	● 149·5	●
7	10	● 103	(● 96)	● 148·5	●

Table 2 lists the transition temperatures of compounds with different numbers of benzoyloxy groups in the lateral part of the molecule. These examples demonstrate the transition from the lateral aryl substituted compound **8** [18] to the twins **5** and **9**. Addition of a benzoyloxy group increases the clearing temperatures by about 45 K.

Table 2. The transition from lateral aryl substituted mesogen to novel twins; transition temperatures are in °C.

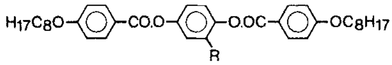


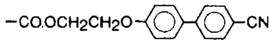
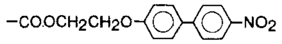
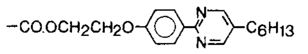
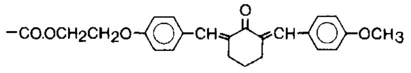
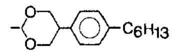
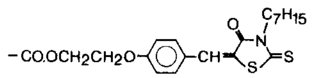
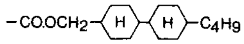
No.	*n*	C	S_C	N	I	
8	0	● 85	(● 67)	● 104	●	[18]
5	1	● 99	(● 88·5)	● 151·5	●	
9	2	● 130	–	● 197	●	

In compound **9** the clearing temperature is higher than that of the unsubstituted phenylene-1,4-bis-(4-*n*-octyloxybenzoate), namely 194·9°C.

Table 3 gives further examples for compounds of the novel type D. In order to allow a better comparison the basic mesogen has been kept constant, only the lateral mesogenic moieties being changed. In the biphenyl derivatives **10** and **11** the S_A phase dominates because of the strongly polar nitro and cyano substituents. In the lateral aryl substituted liquid crystals we have already found and discussed an analogous relationship [19]. The nematic phases of the phenylpyrimidine **12** and the cyclohexanone derivative **13** can be supercooled to room temperature. According to our structure concept the lack of the spacer in the phenyldioxane derivative **14** strongly suppresses the mesomorphic properties. The benzylidene rhodamine derivative **15** is the only known twin with the polymorphism S_C, S_A. In the compound **16** the lateral mesogen contains alicyclic rings. These examples demonstrate the advantages of our structure concept for the convenient synthesis of non-symmetric twin compounds.

Table 3. Phase behaviour of lateral–terminal linked twin molecules of the type D; transition temperatures are in °C.



No.	*R*	C	S_C	S_A	N	I
10		● 102	-	● 192	● 194	●
11		● 97	-	● 196	-	●
12		● 124	-	-	● 167	●
13		● 142	-	-	● 194	●
14		● 79	-	-	(● 40)	●
15		● 109	● 131	● 175	-	●
16		● 106	(● 84)	-	● 154	●

The clearing temperature is determined by the structures of the mesogenic units as well as the nature and the length of the spacers. The coincidence of the clearing temperatures of compounds **9–11** and **13** with that of the basic compound hydroquinone bis-(4-*n*-octyloxybenzoate) is by chance and is not a limiting value which could not be exceeded.

With the exception of **14** the compounds can be synthesized by reaction of the appropriate intermediate product containing a hydroxy group with 2,5-bis-(4-*n*-octyloxybenzoyloxy)-benzoylchloride. The reaction of the same acid chloride with the appropriate bifunctional intermediates yields lateral–lateral bound twins of type E.

In compounds **17–25** (see table 4) two three-ring mesogens are bound by a flexible aliphatic spacer. Figure 1 shows the transition temperatures of a homologous series

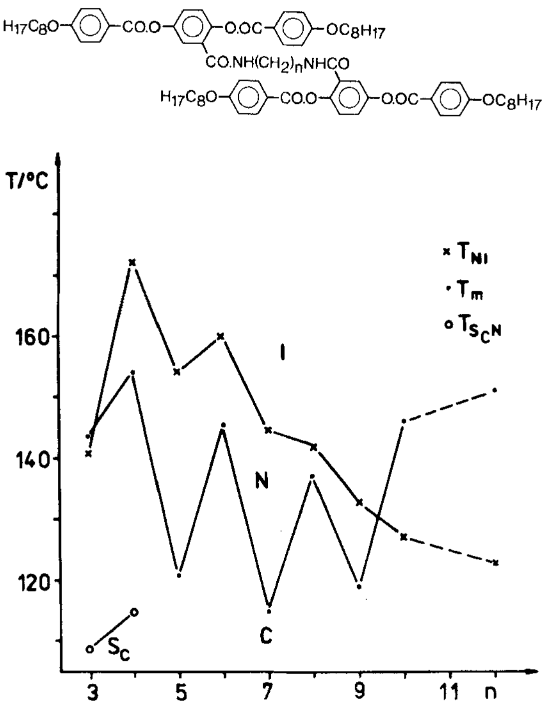
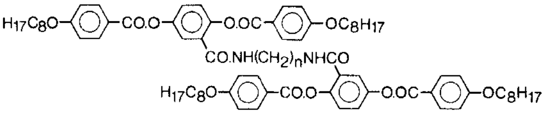


Figure 1. Phase behaviour in the homologous series of the α,ω-bis-[2,5-bis-(4-*n*-octyloxybenzoyloxy)-benzamido]-alkanes; (compounds **17–25**).

Table 4. α,ω-Bis[2,5-bis(4-*n*-octyloxybenzoyloxy)-benzamido]-alkanes; transition temperatures are in °C.



No.	*n*	C	S_C	N	I
17†	3	● 143	(● 109	● 141)	●
18	4	● 154	(● 115)	● 172·5	●
19	5	● 121	(● 80·5)	● 154	●
20	6	● 145·5	–	● 160	●
21	7	● 115	–	● 144·5	●
22‡	8	● 137	–	● 142	●
23	9	● 119	–	● 132·5	●
24	10	● 146	–	(● 127)	●
25	12	● 151	–	(● 123)	●

D.S.C. investigation:

† ΔH_m = 48·7 kJ mol^{-1}, ΔH_{NI} = 3·49 kJ mol^{-1}, glass transition at 41°C, ΔC_p = 122 J mol^{-1} K^{-1}.

‡ ΔH_m = 85·0 kJ mol^{-1}, ΔH_{NI} = 3·40 kJ mol^{-1}, no glass transition above room temperature.

resulting from the increasing length of the alkyl chain of the spacer. All of the compounds are nematic and the lower members exhibit, additionally, monotropic S_C phases. The alternating clearing curve shows a decreasing trend. The melting temperatures alternate in the same sense, although this is much more pronounced.

In compound **17** a transition to a nematic glass has been observed above room temperature. This transition is indicated by a typical decrease of the heat capacity in the D.S.C. run at decreasing temperature. As the investigation of compound **22** proves that this transition temperature is lower in the higher members of the series.

The spacer connecting the two mesogens may contain cyclic segments without loss of the liquid-crystalline properties. In table 5 some examples of this kind are listed. Starting from our structure concept that the three-ring compound and the lateral cyclic segment should be connected by an odd spacer, we have synthesized by double use of this principle the mesogens **26–31** which possess high clearing temperatures. The phenyl ring localized in the spacer may be laterally substituted itself, as several examples in table 5 prove.

Compared with the phenylene compound **26** the chloro and methyl substituent in compounds **27** and **28** respectively causes a depression of the clearing temperature by about 15 K, and the ethyl group in **29** causes one of 29 K. These values are markedly lower than those obtained by lateral substitution of the 1,4-phenylene-bis-(4-*n*-octyloxybenzoates) with the same substituents [2]. The relatively small disturbing effect of the lateral substituents is emphasized by the mesogenic properties of **31** with a 2,5-dimethoxy-1,4-phenylene segment in the spacer.

The cyclic segment in the spacer may be modified in many ways by different substituents as well as by the use of alicyclic and heterocyclic ring systems. A further aspect is indicated by compound **32**. Here the spacer contains a moiety which is mesogenic itself. Comparing **26** with **32** it can be seen that the exchange of a 1,4-phenylene ring by a biphenyl-4,4′-ylene segment enhances the clearing temperature by 19 K. The syntheses and properties of such mesogenic triplets will be published elsewhere [20].

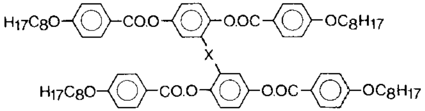
Another feature of compounds of type E is worth mentioning. As the results listed in table 5 prove, these substances tend to have glass transitions at about room temperature. The glass transitions have been detected by D.S.C. investigations which show typical jumps in the heat capacity curves. Also microscopic inspection proves the existence of a rigid birefringent medium with typical nematic textures at temperatures below T_g.

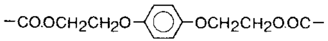
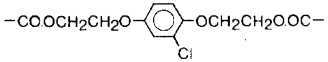
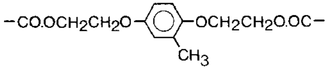
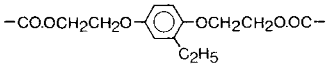
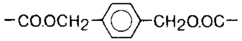
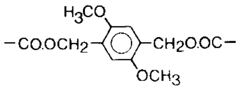
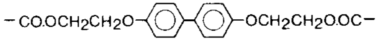
2.2. *X-ray investigations*

Since the time of Vorländer [1] it has been known that the constituent molecules of calamitic liquid crystals should have an elongated rod-like shape. The mesomorphic behaviour of compounds with long lateral substituents can be explained by assuming an approximately parallel orientation of the lateral substituents with respect to the long axis of the basic molecule. The novel twin compounds (see tables 4 and 5) deviate markedly from the classical rod-like shape, so a straightforward explanation of their mesomorphic properties is not possible.

In order to obtain information about the structure of the nematic phases and the effective molecular shapes we have performed X-ray investigations on the nematic phases of several twin compounds. The investigations have been performed with a flat film method using oriented samples. The orientation was achieved with varying

Table 5. Phase behaviour of lateral–lateral linked twin molecules with substituted and unsubstituted 1,4-phenylene segments in the spacer; transition temperatures are in °C.



No.	X	Microscopic data					D.S.C. investigation			
		C		N		I	ΔH_m/kJ mol^{-1}	ΔH_{NI}/kJ mol^{-1}	T_g/°C	ΔC_p/J K^{-1} mol^{-1}
26		●	135	●	159	●	55·3	5·02	16	550
27		●	127	●	145	●	69·2†	3·38	12	554
28		●	125	●	144	●	45·8	4·67	12	370
29		●	108	●	130	●	43·2	3·84	10	560
30		●	120	●	158	●	–	–	-	–
31		●	142	(●	130)	●	75·7	3·54	17	300
32		●	113	●	178	●	50·7	4·25	21	475

† Two melting peaks; cooling rates: 40 K min.

‡ Almost no crystallization during heating; heating rates: 20 K min.

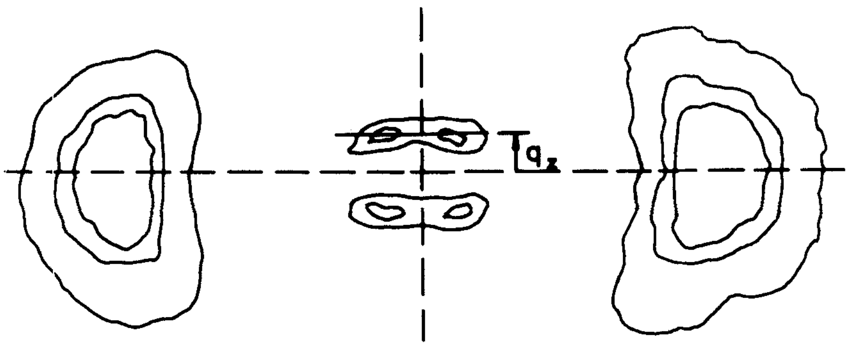


Figure 2. Schematic representation of an X-ray pattern for the nematic state of compounds **17–25**.

success by means of a magnetic field (about 1·5 T). In well oriented samples a pattern, sketched in figure 2, was obtained. The scattering vector, **q**, of the four diffuse spots, its component in the z direction, q_z (which is the direction of the magnetic field), and its angle with the z direction have been evaluated. The q_x vector corresponding to the outer diffuse scattering on the equator does not show any pecularities compared with conventional mesogenic substances.

Compounds **17–25**

In some members of this series a strong tendency to decompose during the investigation was found; however, typical X-ray patterns were maintained. The patterns suggest the appearance of skewed cybotactic groups [21], especially in the low temperature range of the nematic phases. The tilt angle between the building units (twins) of the groups and the normal to the groups has been estimated to be about 39° in all members. Furthermore, the thickness of the cybotactic groups and therefore also the lengths d' of the constituent units (measured by q_z) have been found to be independent of the length of the spacer. A value of 3·45 nm was obtained for d'. These experimental results require a model of the molecule in which the linking alkyl chains do not influence the effective length of the twin. However, value of d' is incompatible with the length of one half of the twin. The molecular model shown in figure 3 should

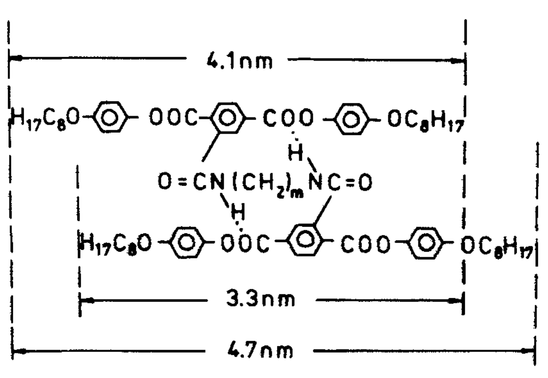


Figure 3. Molecular model of compounds **17–25** in the nematic phase.

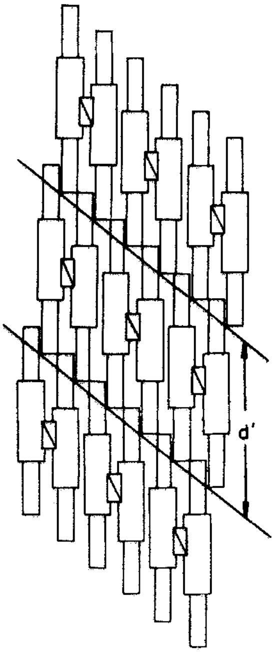


Figure 4. Structural model of cybotactic groups. The symbol ⧅ denotes the bridge.

account for our observations. We assume that the proposed effective molecular shape is stabilized by hydrogen bonds between the amino group of the bridge and the carboxylic group of the opposite part of the molecule. The linking alkyl chains are assumed to be arranged outside of the twin plane in a ball-like conformation. A structural model of the nematic phase (see figure 4) constituted of these building units and based on a dense packing contains the observed density period and explains the appearance of the cybotactic groups. The shortening of the period d' with respect to the shortest molecular length is caused by the interdigitation of the terminal alkyl chains.

Compounds **26**, **27**, **29** *and* **32**

The X-ray patterns of these compounds contain a very similar feature as described for **17–25**. The q_z vector in the nematic phase of **25** gives a value of 3·7 nm, independent of the temperature. The corresponding length can be found in the molecular model as sketched in figure 5. This conformation of the molecule is based on the assumption that the aromatic moieties of the two halves of the molecule as well as of the bridge are oriented nearly parallel to each other. Reduction of the length of the bridge by eliminating one benzene ring gives a reduction of d' by 0·3 nm. A dense packing of these twins with an associated interdigitation leads to a structural model that is very similar to that described in figure 4.

Summarizing, we can conclude that the molecules of the twins which are bound lateral–lateral by long spacers exist in the nematic phase in a special conformation which allows us to recognize the trend to an effective rod-like shape. Nevertheless, the

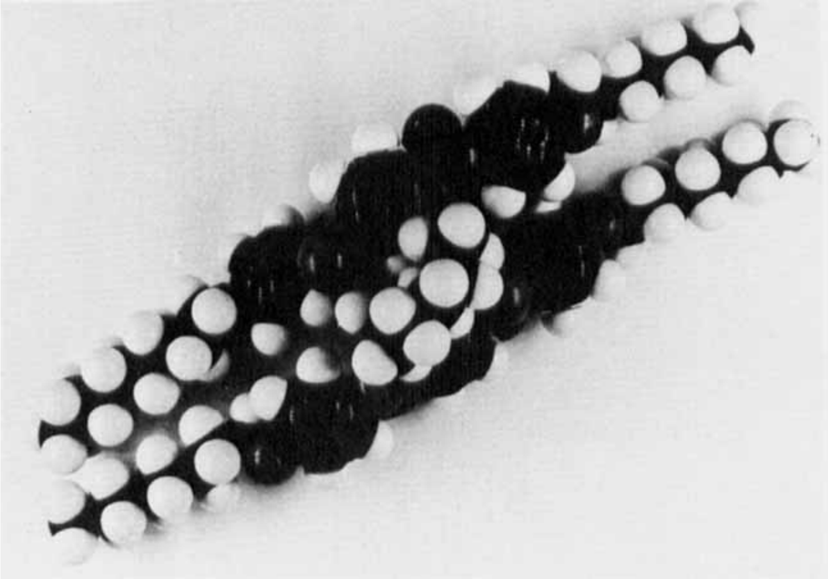


Figure 5. Molelcular model of compound **25**.

deviations from the classical rod-like shape are so strong that the explanation of the nematic state of these compounds does not seem possible by means of the molecular statistical theories for rod-like molecules [22]. The molecular statistical theories which in the present state include rod-like molecules as well as disc-like species [23] need a further extension to lath-like compounds.

There are twins consisting of two disc-like moieties linked by various spacers [24, 25]. In contrast with the results in our new compounds, the spacers in these substances possess elongated conformation [24, 25].

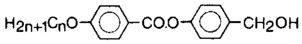
Appendix

Synthesis of the compounds

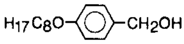
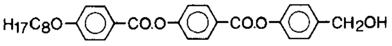
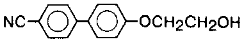
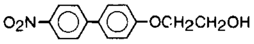
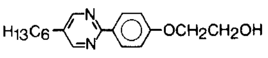
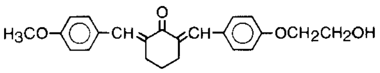
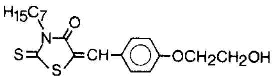
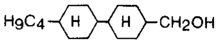
The reaction of 2,5-bis-(4-*n*-octyloxybenzoyloxy)-benzaldehyde [26] with 2-(4-*n*-hexylphenyl)-propane-1,3-diol yields compound **14**. All other compounds have been obtained by acylation of the appropriate hydroxy or amino substituted components with 2,5-bis(4-*n*-octyloxybenzoyloxy)-benzoylchloride [18]. The α,ω-diamines needed for the synthesis of substances **17**–**25** are commercially available. The melting temperatures of the new intermediate products are listed in table 6.

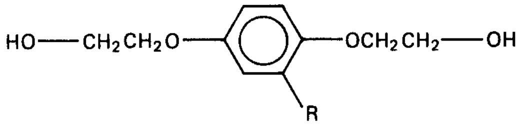
The substituted benzylalcohols **1a**–**9a**, **16a**, **30** and **31a** can be obtained by reduction of the corresponding formyl compounds with sodium borohydride. The substituted phenoxyethanols **10a**–**12a**, **26a**–**29a** and **32a** have been synthesized using known routes by reaction of phenols with chloroethanol in alkaline medium. Compound **13a** has been produced by condensation of 2-(4-methoxybenzylidene)-cyclohexanone with 4-(2-hydroxyethoxy)-benzaldehyde. The reaction of the same aldehyde with 3-*n*-heptyl-4-oxo-thiazolidine-2-thione [27] yielded **15a**. The esterification of the intermediates with 2,5-bis-(4-*n*-octyloxybenzoyloxy)-benzoylchloride was performed in toluene by addition of triethylamine and catalytic amounts of 4-dimethylaminopyridine.

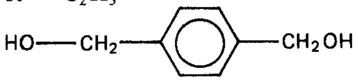
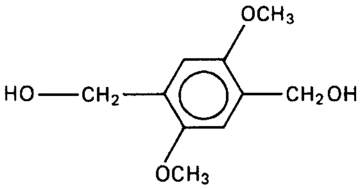
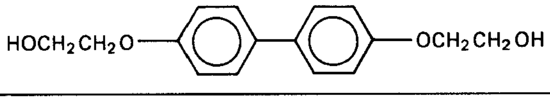
Table 6. Phase behaviour of intermediate products (the numbers are given in relation to the end products with the designation 'a'). Temperatures are in °C.



	n	Melting point/°C
1a	4	100
2a	5	85
3a	6	84
4a	7	81·5
5a	8	85
6a	9	84
7a	10	84·5

8a		C 48 I
9a		C 148 N 199 I
10a		C 127·5 (N 126) I
11a		m.p. 131
12a		m.p. 76
13a		C 144 N 181 I
15a		m.p. 97
16a		m.p. 133



26a	R = H	m.p. 107
27a	R = Cl	m.p. 70
28a	$R = CH_3$	m.p. 85
29a	$R = C_2H_5$	m.p. 58
30a		m.p. 119
31a		m.p. 165
32a		m.p. 217

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