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Influence of lateral substituents on the mesophase behaviour of banana-shaped mesogens†

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In this paper we present selected members of 7 new series of bent-shaped five-ring resorcinol derivatives which are distinguished by substituents at the central core as well as at the outer rings. Depending on the kind and position of the substituents and depending on the length of the terminal chains not only have new mesophases (the C_{PA} phase or three unidentified B_2-like phases) been identified, but also interesting phase sequences have been observed (B_2–N; B_2–SmA; B_2–SmA–SmC; B_2–SmA–SmC–N).

Introduction

The term "banana-shaped mesogens" is used as a synonym for a new field of liquid crystals; this field was established by the lecture and the corresponding paper of Takezoe at the 6th International Liquid Crystal Conference 1996 in Kent, Ohio.[1] He reported ferroelectric properties of a new type of mesophase which is formed by non-chiral bent mesogens. This discovery was the beginning of a lot of activity to investigate the structure and properties of these new mesophases which are not comparable with smectic phases formed by calamitic mesogens.

Up to now at least seven phases have been described and preliminarily designated by the code letters B_1–B_7.[2,3] The B_1 phase exhibits a two-dimensional order. There are strong arguments that it will be necessary to subdivide phase B_1 into modifications with different columnar structure.[4] The B_2 phase corresponds to the phase first discussed by Takezoe *et al.*[1] and is of special interest because it shows antiferroelectric behaviour.[5] A second phase which can be electro-optically switched in a similar way was named as the B_5 phase.[6] The phases B_3 and B_4 are crystalline-like modifications, the B_4 phase is also designated as the "blue phase".[7–9] The B_6 phase can be compared with an intercalated smectic C phase, but it is generated by bent molecules.[3] The growing of the B_7 phase on a slow cooling of the isotropic phase is accompanied by impressive optical pictures. Myelinic textures, ribbons, spirals and other figures give strong hints for a helical superstructure,[10,11] but the phase structure is unknown up to now. It should be emphasised that all B-phases (with exception of the B_3 and B_4 phases) have layer structures without in-plane order.

General remarks on structure–property relationships of banana-shaped mesogens

A sufficient pool of substances is an important precondition for extensive physical measurements. However, the specific synthesis of bent mesogens was started only a few years ago. As shown by different research groups, the connections between the chemical structure of bent molecules and their mesophase behaviour are not comparable to those known from calamitic mesogens. Therefore, basic research has to be done in the field of banana-shaped liquid crystals in order to facilitate the design of new compounds exhibiting the desired mesophase behaviour. Starting from the general formula, different possibilities for variation of the chemical structure may be considered as can be seen in Chart 1.

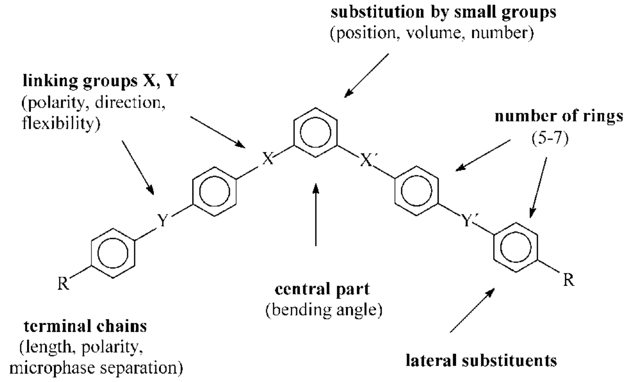

Chart 1

Most banana-shaped liquid crystals described up to now correspond to this general formula and they contain five phenyl rings, the bending angle results from a central 1,3-phenylene unit. But also the 2,7-disubstituted naphthalene unit is a suitable *central part*.[12] Compounds with six or seven aromatic rings have also been reported.[13–15] With an increasing *number of rings* the transition temperatures increase. Four-ring compounds seem not to be able to form B-phases. The exchange of phenyl rings with six-membered heterocyclic rings like pyridine or pyrimidine was reported for seven-ring compounds.[14] The substitution of the central ring by a five-membered heterocycle like 2,5-disubstituted 1,3,4-thiadiazole or 1,3,4-oxadiazole results in nematic or smectic mesophases, which are typical for calamitic liquid crystals.[16,17] The reason for this is still not clear. The bending angle, for example, of the latter heterocyclic fragment is theoretically about 135°, which should be sufficient for a polar packing to form B-phases. On the other hand, Dingemans *et al.*[18] found new mesophases for boomerang-shaped mesogens, which contain five-membered heterocyclic units. The phase type could not be assigned because of the high transition temperatures.

Alkyl and alkyloxy chains were used as *terminal groups* in banana-shaped mesogens in most cases. Only a few complete

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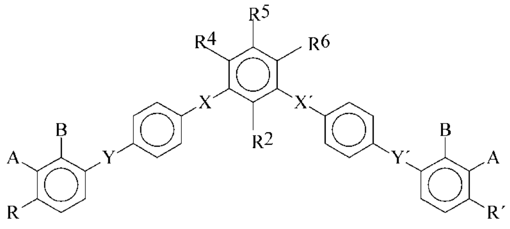
homologous series have been synthesised up to now. The trend of the clearing points is very different in these series. With a growing number of carbon atoms in the chain the transition temperatures B-phase → isotropic phase can increase as well as strongly decrease and they can also be nearly independent of the chain length.[3] Systematic investigations need to be carried out to investigate these relationships. Often, the following tendency can be observed. Short-chain homologues exhibit a nematic phase, smectic phases or the B_6 phase. Derivatives with terminal chains of medium length can show B_1 or B_2 phases. With an increase in the length of the terminal groups, the existence of the B_2 phase is more probable. The larger the mesogenic core, the longer the alkyl chains have to be in order to obtain B_2 phases. Often, the trend for the clearing temperatures is unusual. In contrast the corresponding curves for a homologous series of calamitic liquid crystals show a more continuous slope of the transition temperatures, that is, the clearing curve B_1–isotropic passes through a maximum and after that strongly decreases. The longer chain derivatives exhibit a transition B_2–isotropic, the clearing temperatures increase again.[19,20]

The terminal carbon–hydrogen chains can also be linked by sulfur,[21] carbonyl[7] or carboxylic groups.[7,22] The influence of the electronic properties of these terminal substituents on the mesophase behaviour has not been investigated in detail and seems to be related to the type and direction of the connecting groups between the aromatic rings. The introduction of perfluoroalkyl fragments is accompanied with a strong increase in the transition temperatures.[13,23] Three-ring compounds generated by the reaction of resorcinols with 4-(perfluoroalkylmethoxy)benzoic acids exhibit liquid crystalline properties, however only smectic phases could be detected.[24]

The effect of the *connecting groups X, Y* on the liquid crystalline behaviour of banana-shaped compounds is unusually strong in comparison with calamitic mesogens.[3] Simple inversion of the linking groups X or Y resulting in isomeric compounds can cause a very different mesophase stability and can even lead to the loss of liquid crystalline properties. This behaviour cannot be explained in terms of our knowledge of rod-like mesogens.[25] However, one possible explanation could result from the special packing of the bent molecules within the layers. According to Bedel *et al.*[26] an alternating distribution of the electron density throughout the molecules leads preferentially to B-phases. The removal of two connecting groups will reduce the conformational flexibility which seems to disfavour B-phase formation, as shown by Shen *et al.*[14] for *m*-terphenyl derivatives and other compounds. The linkage of two three-ring fragments by means of single units like CH_2, CO, S, O was investigated by Thisayukta *et al.*[27]

The introduction of *lateral substituents* into different positions of calamitic and discotic mesogens is a common procedure in the field of liquid crystals in order to change the polymorphic behaviour as well as the structure of the mesophases. The depression of the melting points is another important reason for use of lateral groups. With rod-like molecules, the attachment of lateral substituents decreases the length-to-breath ratio and therefore the clearing temperatures. However, the enlargement of lateral groups can lead to new liquid crystalline phases which result from a special packing of the molecules with a non-conventional molecular shape in smectic layers.[28]

Banana-shaped mesogens can be laterally substituted by atoms or small groups only in a limited way, depending on the number of aromatic rings. One has to distinguish between the substitution at the central phenylene ring and that at the outer rings, and in both cases the position of lateral substituents is of great influence. These two substitutions are basically different, because the substituents near the linking groups of the central part can change the bending angle between the two legs of the molecules. Systematic studies performed in the parent series of five-ring banana-shaped mesogens prove the sensitivity of such compounds to lateral substituents attached to the central ring. Groups like cyano, methyl or methoxy at the top of the bent molecules, that is in position R^5, prevent the existence of any mesophases.[29] However, substitution of the 5-position by a methoxycarbonyl group is accepted without loss of the liquid crystalline properties if perfluoroalkyl groups exist in the terminal positions.[23] In contrast, the introduction of small groups like methyl or nitro into the obtuse angle of the molecules, *i.e.* in position R^2, results in a high mesophase stability. For example, the B_5 phase was detected with 2-methyl substituted derivatives.[6] The 2-nitro substituted homologues exhibit the B_7 phase up to about 175 °C, and these clearing temperatures are comparable with those of the non-substituted parent molecules.[30] One chlorine atom in the 4-position results in substances having a B_2 phase.[31] It should be mentioned that the corresponding terminally alkyl-substituted derivatives are the subject of many physical measurements because the temperature range of the B_2 phase is 70–120 °C.[32–35] The additional introduction of a second chlorine atom into the position R^6 causes a change of the type of mesophase from the B-phase to nematic and smectic phases.[36] This surprising behaviour could be explained after a closer examination of the conformation of the molecules. As proved by NMR investigations performed in the liquid crystalline state, the bending angle between the two half-parts of the bent molecules is changed by substituents which are situated near the connecting groups. Thus, the bending angle of about 120°, expected for the 1,3-phenylene unit, was found for the parent molecules which are unsubstituted at the central ring. This bending angle is increased by the 4-chloroatom to 134° and by two chlorine atoms in 4,6-positions to about 165°. In the latter case, the molecules exhibit a rather rod-like conformation, therefore the existence of phases which are typical for calamitic mesogens is not surprising. The nearly stretched conformation was also observed in the crystalline state.[37] Matraszek *et al.*[38] found nematic phases with 4-*n*-hexylresorcinol derivatives on supercooling.



Generally the substituents attached to the central aromatic unit make it possible to vary the bending angle in a delicate way. Thus, for the first time the phase sequences SmA–SmC–B_2 and N–SmA–SmC–B_2 were found with 4-cyano-substituted resorcinol derivatives.[39,40]

The 4-bromoresorcinol derivatives are not liquid crystalline, whereas the 4-bromoterephthalic acid esters exhibit mesophases up to high temperatures.[41] This again illustrates why the discussion of substituent effects has to be related to the chemical structure of the whole molecule.

The lateral substitution of the outer phenyl rings of five-ring banana-shaped mesogens has been started by several groups. The introduction of fluorine or chlorine near the terminal wing groups was reported by Heppke *et al.*,[42] Lee and Chien[43,44] and Bedel *et al.*[26] Beside such halogen atoms also a methoxy group was attached at the same position by Kwon *et al.*[45] According to Nguyen *et al.*[46] the mesophase behaviour of compounds containing thioester groups was drastically changed by the introduction of fluorine. Up to four mesophases were found, which could not be assigned, whereas the unsubstituted parent molecules show nematic and smectic phases. Recently, Niori *et al.*[47] studied the influence of lateral substituents attached to different positions of non-symmetric banana-shaped liquid crystals on the mesomorphic properties.

By increasing the number of aromatic rings of the mesogenic core the possibilities of substitution without the loss of the liquid crystalline properties are widened. Mesomorphic properties of fluoro-substituted compounds derived from 2,7-dihydroxynaphthalene were reported by several groups. Reddy *et al.*[19] substituted two of the outer phenyl rings with fluorine, whereas Kozmik *et al.*[48] performed the substitution of the naphthalene unit by fluorine in the 1-position. Recently, six-ring derivatives have been investigated by Dantlgraber *et al.*[49] Here the central biphenyl-3′,4-diyl unit was substituted with fluorine in different positions. Using the same substance class, Rauch *et al.*[50] discussed two electro-optically switchable phases for a compound which is fluoro-substituted at the outer rings. Substituents like fluorine, chlorine and methyl were attached to the rings linked between the central and the outer phenyl fragments of seven-ring compounds. Comparing the influence of chlorine and the methyl group, which have nearly the same van der Waals volume, Sadashiva *et al.*[15,51] reported a behaviour different from that known for calamitic mesogens. A seven-ring compound also substituted in the obtuse angle of the central unit by the nitro group possesses a nematic–B_1 dimorphism at high temperatures.[14]

The main goal of this paper is to study the influence of simultaneous substitution of the central and the terminal phenyl rings on the mesophase behaviour of banana-shaped compounds. For this reason we synthesised new five-ring resorcinol derivatives which exhibit identical connecting groups. For a given substitution of the central ring by Cl, F, CN, CH_3, or NO_2 the position of substituents at the outer rings (F, Cl, CH_3, CF_3) was systematically varied. The introduction of fluorine is of advantage for the characterisation of the structure since not only ^1H or ^{13}C NMR spectroscopy can be performed but also ^{19}F NMR.

Results and discussion

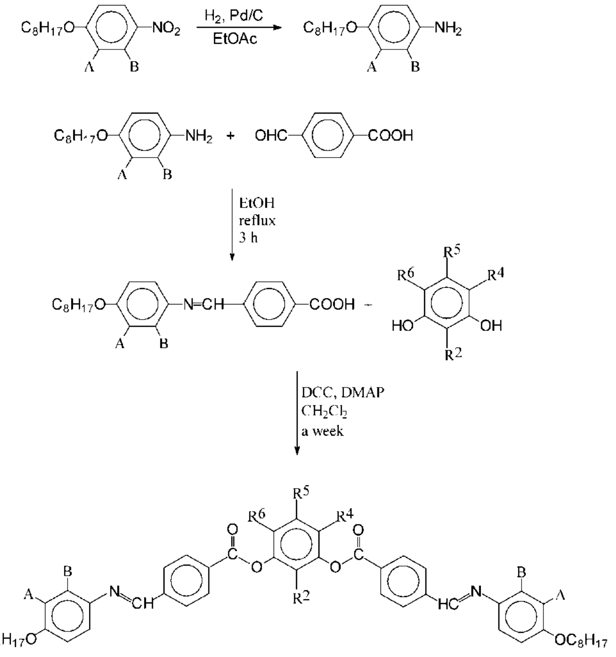
Materials

The synthesis of 1,3-phenylene bis[4-(4-*n*-alkyloxyphenyliminomethyl)benzoates] can be realised using two reaction pathways. 4-Formylbenzoic acid can be esterified with resorcinol to give 1,3-phenylene bis(4-formylbenzoate) which when condensed with the corresponding anilines gives the desired Schiff's bases. As shown in Scheme 1 we preferred the condensation of 4-formylbenzoic acid with the substituted anilines[52,53] in the first reaction step.

The substituted 4-(4-*n*-alkyloxyphenyliminomethyl)benzoic acids **1a**–**i** can be easily purified by recrystallisation. They exhibit nematic and smectic phases up to high temperatures. The phase behaviour is listed in Table 1.

To prepare the final products the two-ring acids **1a**–**i** have to be esterified with the corresponding resorcinols. 2-Methyl-, 2-nitro-, 4-chloro- and 4,6-dichlororesorcinol are commercial materials. Starting from 2,4-dihydroxybenzaldehyde *via* the aldoxime the elimination of water was realised with acetic anhydride, and deprotection of the acetate groups gives the 4-cyanoresorcinol.[40] 5-Fluororesorcinol was prepared by demethylation of the 3,5-dimethoxyfluorobenzene by means of BBr_3 in dichloromethane.[54]

The reaction of the substituted benzoic acids **1a**–**i** with related resorcinols was performed by means of dicyclohexylcarbodiimide in dichloromethane using dimethylaminopyridine as catalyst. The final crude products **2**–**8** were recrystallised from DMF–ethanol. In order to reduce the conductivity, a requirement for dielectric measurements, substances were purified by recrystallisation from toluene–heptane. The phase behaviour of all synthesised substances is summarised in the Tables 2–8.



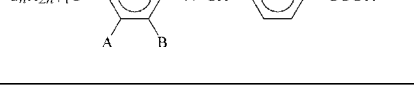
Scheme 1

Compounds that have been described before by other authors or by ourselves are marked by the corresponding references. For the investigations of physical properties reported in this paper, the derivatives previously synthesised by other research groups were prepared by us again.

Mesophase behaviour and physical properties

The introduction of one to four substituents into five-ring bent molecules allows systematic studies of the influence of lateral substituents on the mesophase behaviour of banana-shaped liquid crystals. The central phenylene unit was substituted with fluorine, chlorine, methyl, cyano, nitro groups as well as two chlorine atoms. Fluorine, chlorine, methyl and trifluoromethyl groups were attached at the outer aromatic rings. Depending on the position of substitution and the volume and electronic properties of the substituents the mesophase behaviour can be changed. The question arises which pattern of substitution the molecules accept without loss of the liquid crystalline properties. To allow the comparison of the different effects the

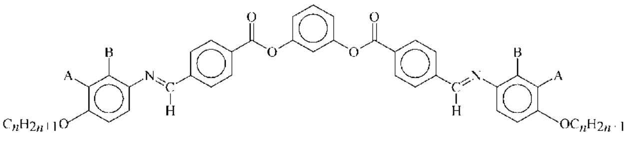
Table 1 Transition temperatures (*T*/°C) of the substituted 4-(4-*n*-alkyloxyphenyliminomethyl)benzoic acids **1a**–**i**



No	N	A	B	Transition temperatures[a]
1a[36]	8	H	H	Cr 183 SmC 258 N 261 I
1b[36]	12	H	H	Cr 155 SmC 255 I
1c	8	F	H	Cr 147 SmX[b] 181 SmC 262 I
1d	12	F	H	Cr 112 SmX[b] 168 SmC 249 I
1e	8	H	F	Cr 192 SmC 239 N 253 I
1f	12	H	F	Cr 165 SmC 237 I
1g	8	Cl	H	Cr 120 SmC 144 N 239 I
1h	8	H	CH_3	Cr 130 SmC 163 N 220 I
1i	8	H	CF_3	Cr 131 N 188 I

[a] Abbreviations: Cr: crystalline solid; SmC, SmA: smectic phases C and A; N: nematic phase, I: isotropic liquid. [b] Preliminary X-ray studies point to a new smectic phase.

Table 2 Phase transition temperatures of the derivatives of resorcinol **2a–i**



No	*n*	A	B	Transition temperatures/°C[a]
2a[30]	8	H	H	B_4 139 B_3 152 B_2 174 I
2b[30]	12	H	H	B_4 141 B_2 170 I
2c[43,44]	8	F	H	Cr 128 B_2 166 I
2d	12	F	H	Cr 119 B_2[b] 161 I
2e	8	H	F	Cr 128 B_2 142 I
2f	12	H	F	Cr 118 B_2 144 I
2g[44]	8	Cl	H	Cr 74 B_2[b] 140 I
2h	8	H	CH_3	Cr 110 (B_2 80) I
2i	8	H	CF_3	Cr 110 (B_2 36) I

[a] Abbreviations: B_2, B_3, B_n: different B phases. [b] Assignment of this phase is not definite, see text.

mesogenic core is the same in all the compounds **2**–**8**. There are several aspects to discuss the influence of substituents.

In the following sections (see Tables 2–8) the substance classes of five-ring banana-shaped liquid crystals are presented where the central phenylene unit remains unchanged but the kind and position of the substituents at the outer rings is varied.

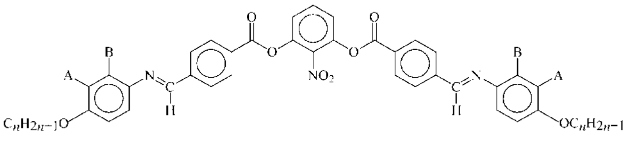
Derivatives of non-substituted resorcinol

All compounds presented in Table 2 exhibit B_2 phases. The derivatives **2a** and **2b** belong to the series reported by Sekine *et al.*[30] in 1997. Starting from the parent molecule **2a** the introduction of fluorine (**2c**) and chlorine (**2g**), respectively, in positions A of the outer rings decreases the clearing temperatures by 8 K and 34 K, respectively. Generally, the reduction of the mesophase stability is greater if the outer rings are substituted in the position B than in position A. (Compare the transition temperatures B_2–isotropic of the compound **2c**, **2d** with those of compounds **2e**, **2f**). It should also be noted that compound **2c** forms a B_4 phase but only after fast cooling.

2-Nitro-substituted resorcinol derivatives

The mesophases of all the compounds derived from 2-nitroresorcinol can be classified as B_7 phases (Table 3). Fig. 1 presents a microphotograph obtained on slowly cooling the isotropic phase of compound **3g**. It shows two-dimensional patterns and myelinic domains typical for the B_7 phase. In Fig. 2 the X-ray pattern of a non-oriented sample of the same substance is shown, characterised by several peaks in the small-angle region which are not commensurable to each other. A voltage up to 18 V μm^{-1} is not able to switch the phase electro-optically. The textures give hints for a helical superstructure of the B_7 phase, however, it should be pointed out that its phase structure is unknown up to now.

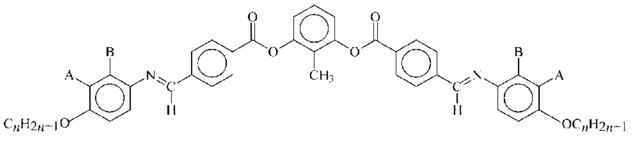
Table 3 Phase transition temperatures of the derivatives of 2-nitroresorcinol **3a–i**



No	*n*	A	B	Transition temperatures/°C
3a[10]	8	H	H	Cr 87 B_X 129 B_7 177 I
3b[10]	12	H	H	Cr 85 B_7 173 I
3c	8	F	H	Cr 147 (B_X 142) B_7 169 I
3d	12	F	H	Cr[a] B_7 168 I
3e	8	H	F	Cr 81 B_7 157 I
3f	12	H	F	Cr 88 B_7 156 I
3g	8	Cl	H	Cr 117 B_7 148 I
3h	8	H	CH_3	Cr 137 I
3i	8	H	CF_3	Cr 140 I

[a] Melting point could not be detected.

Table 4 Phase transition temperatures of the 2-methylresorcinol derivatives **4a–i**



No	*n*	A	B	Transition temperatures/°C
4a[6]	8	H	H	Cr 161 B_5 165 B_2 172 I
4b[6]	12	H	H	Cr 148 B_2 164 I
4c	8	F	H	Cr 129 (B_{X3} 111) B_{X2} 136 B_{X1} 153 I
4d	12	F	H	Cr 122 (B_{X3} 114 B_{X2} 119) B_{X1} 150 I
4e	8	H	F	Cr 135 (B_1 135) I
4f	12	H	F	Cr 125 B_2 135 I
4g	8	Cl	H	Cr 93 B_2 127 I
4h	8	H	CH_3	Cr 130 I
4i	8	H	CF_3	Cr 113 I

In search for substances with low transition temperatures for B_7–I, the halo-substituted compounds are more suitable because the clearing temperatures are reduced below 150 °C. On the other hand, introduction of CH_3 or CF_3 into the position B prevents mesophases.

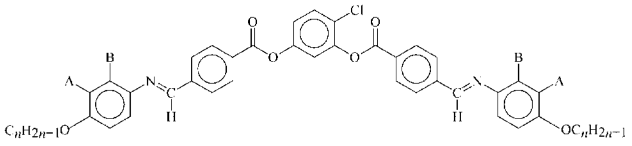
For compound **3a** and **3c** a transition of the B_7 phase into a low-temperature phase (preliminarily designated as B_x) could be detected by calorimetry and dielectric measurements but no change of the texture could be recognised at this transition.[55,56] Also the X-ray patterns point to a more continuous change into a higher ordered phase.

Derivatives of 2-methylresorcinol

In the homologous series of 2-methylresorcinol derivatives the B_2–B_5 dimorphism was detected for the first time (Table 4).[6] The electro-optical behaviour of both mesophases is similar. In comparison to the B_2 phase the B_5 phase exhibits an additional in-plane order, and it still has short range order character.

By shortening the terminal chains, for the first time a B_1 phase appears instead of a B_2 phase on a 2-methylresorcinol

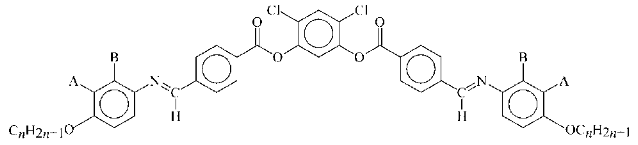
Table 5 Phase transition temperatures of the derivatives of 4-chlororesorcinol **5a–i**



No	*n*	A	B	Transition temperatures/°C
5a[31]	8	H	H	Cr 120 B_2 133 I
5b[31]	12	H	H	Cr 115 B_2 142 I
5c	8	F	H	Cr 90 B_2 133 I
5d	12	F	H	Cr 81 B_2 133 SmA 139 I
5e	8	H	F	Cr[a] 71 B_2 99 N 103 I
5f	12	H	F	Cr 64 B_2 112 I
5g	8	Cl	H	Cr 67 B_2 106 I
5h	8	H	CH_3	Cr 99 (SmC 76) I

[a] Second heating trace from DSC.

Table 6 Phase transition temperatures of the derivatives of 4,6-dichlororesorcinol **6a-i**



No	n	A	B	Transition temperatures/°C[a]
6a[36]	8	H	H	Cr 126 N 148 I
6b[36]	12	H	H	Cr 111 SmC 113 SmC 121 N 137 I
6c	8	F	H	Cr 125 SmA 129 I
6d	12	F	H	Cr 103 (B_2 100) SmC 125 SmA 141 I
6e	8	H	F	Cr 141 (N 128) I
6f	12	H	F	Cr 103 (SmC 85) N 116 Is
6g	8	Cl	H	Cr 117 (B_2 71 SmC 91 SmA 104 N 109) I
6h	8	H	CH_3	Cr 121 (N 105) I
6i	8	H	CF_3	Cr 116 (SmC 56)[b] I

[a] Abbreviations: SmC: smectic C phase with an undulated structure.
[b] Assignment only by polarising microscopy.

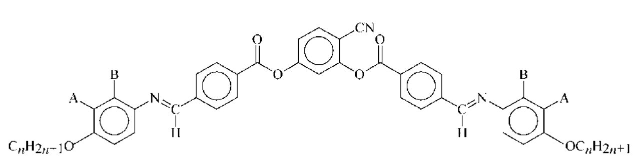
derivative, compare compounds **4f** and **4e**. This is a general trend which was also observed in other homologous series.[13,19,20,30]

If fluorine is attached to the positions A of the basic molecule a mesomorphic trimorphism results, see compounds **4c** and **4d**. The phase transitions are indicated by calorimetry and by polarising microscopy. But the three mesophases could not be identified up to now. First preliminary electro-optical investigations indicate that there are no significant differences in the switching behaviour of the three mesophases B_{X1}, B_{X2}, and B_{X3}, this is similar to that of B_2 phases. In order to study this interesting phase behaviour in more detail we will perform X-ray measurements on oriented samples, in addition to NMR, dielectric and electro-optical measurements. The results will be published in a forthcoming paper.

It is interesting that replacement of fluorine (**4c**) by chlorine in the positions A leads to a strong depression of the clearing point and to the disappearance of two mesophases, see compound **4g**.

4-Chlororesorcinol derivatives

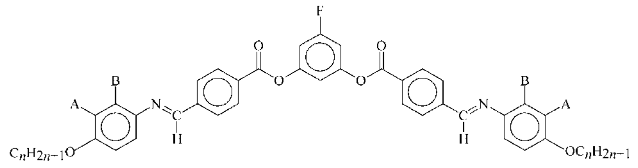
Table 7 Phase transition temperatures of the derivatives of 4-cyanoresorcinol **7a–i**



No	n	A	B	Transition temperatures/°C
7a[40]	8	H	H	Cr 97 B_2 142 SmC 146 SmA 175 I
7b[40]	12	H	H	Cr 65 B_2 122 SmC 141 SmA 188 I
7c	8	F	H	Cr 73 C_{PA} 145 SmA 176 I
7d	12	F	H	Cr 75 B_2 129 SmC 133 SmA 182 I
7e	8	H	F	Cr 95 SmC 97 SmA !02 N 131 I
7f	12	H	F	Cr 94 SmC 126 SmA 142 I
7g	8	Cl	H	Cr 91 B_2 105 SmC 117 SmA 156 I
7h	8	H	CH_3	Cr 90 (B_2 79) SmA 107 I
7i	8	H	CF_3	Cr 127 (B_2 45)[a] I

[a] Assignment by optical textures only, B_2 phase or SmC phase is possible.

Table 8 Phase transition temperatures of the derivatives of 5-fluororesorcinol **8a–g**



No	n	A	B	Transition temperatures/°C
8a	8	H	H	Cr 150 B_2 180 I
8b	8	F	H	Cr 112 B_X 131 $B_{2'''}$ 135 $B_{2''}$ 140 $B_{2'}$ 164 I
8c	12	F	H	Cr 87 B_X 113 $B_{2'''}$ 124 $B_{2''}$ 128 $B_{2'}$ 157 I
8d	8	H	F	Cr 144 I
8e	12	H	F	Cr 140 B_2[a] 142 I
8f	8	Cl	H	Cr 85 B_2 138 I
8g	8	H	CH_3	Cr 117 I

[a] Assignment only by texture observations.

With one exception (compound **5h** which shows a metastable SmC phase) all 4-chlororesorcinol derivatives listed in Table 5 exhibit a B_2 phase. It should be noted that the B_2 phase of compound **5g** forms screw-like domains similar to compound **2c**.

The most interesting materials are compounds **5d** and **5e**. Compound **5d** displays mesomorphic dimorphism B_2–SmA which has been found for only a few substances up to now.[24,40] Compound **5e** is the first example where the B_2 phase is directly formed from the nematic phase. This unusual case will be described in detail below.

Fig. 1 Texture of the B_7 phase of compound **3a** (170 °C).

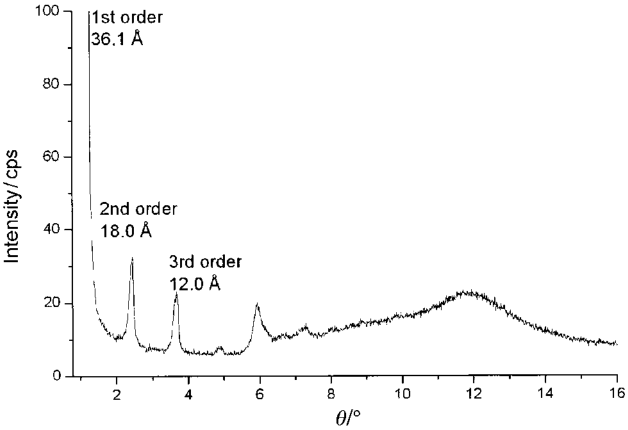


Fig. 2 X-Ray pattern of the B_7 phase of compound **3g** (115 °C).

4,6-Dichlororesorcinol derivatives

4,6-Dichlororesorcinol derivatives reported up to now do not form B-phases because the introduction of two chlorine atoms into the 4,6-positions of the central core gives rise to an increase of the bending angle up to 165° and these compounds can be considered like calamitic compounds.[36] Therefore it is not surprising that most of the compounds listed in the Table 6 form mesophases typical of calamitic mesogens: N, SmA, or SmC. But there are two interesting exceptions. Compound **6d** with the fluorine substituent in position A shows the phase sequence B_2–SmC–SmA with decreasing temperature where the B_2 phase is monotropic. Another interesting material is compound **6g** which is substituted by chlorine in position A. In this case not only do SmA, SmC and B_2 phases occur but a nematic phase is also present. Although all four mesophases are monotropic they could be supercooled and physical investigations could be performed without problems. For both compounds (**6d** and **6g**) electro-optical measurements reveal an antiferroelectric ground state of the B_2 phase with "racemic" or "homochiral" domains which could be switched into ferroelectric states. In the case of compound **6g** relatively large domains with uniform handedness could be observed. It should be mentioned that compound **6g** is the second material where the tetramorphism B_2–SmC–SmA–N was found. The first time, this phase sequence was reported for a cyano-substituted banana-shaped mesogen.[40]

4-Cyanoresorcinol derivatives

Banana-shaped five-ring resorcinol derivatives which are substituted by a cyano group in position R^4 of the central core were the first mesogens which form a B_2 phase characteristic for a bent molecular shape together with the SmA and SmC phases characteristic for calamitic compounds.[39,40] It is seen from Table 7 that this phase behaviour can be also observed if fluorine (**7d**) or chlorine (**7g**) is attached at the positions A. The introduction of a methyl group into the positions B causes a strong reduction of the mesophase stability in comparison to substituents in positions A (**7h**, **7i**). Surprisingly, for compound **7h** the phase sequence B_2–SmA could be detected.

The existence of the C_{PA} phase detected for compound **7c** will be discussed below.

5-Fluororesorcinol derivatives

The common feature of the resorcinol derivatives shown in Table 8 is a fluorine atom in position R^5 of the central core. These are the first five-ring banana-shaped mesogens (without terminal perfluoroalkyl groups) bearing the substituent at the top of the molecule, with liquid crystalline properties. In comparison with the corresponding non-fluorinated compounds the clearing temperatures are not markedly changed (compare compounds **2** with compounds **8**). It is obvious that by additional substitution in the A-position the mesophase stability is somewhat reduced (compare compound **8a** with **8b**, **8f**). By introduction of a substituent into the positions B the mesomorphic properties can disappear. While compound **8a** and **8f** form a B_2 phase only, compounds **8b** and **8c** show mesomorphic tetramorphism. Mesomorphic tetramorphism is also reported in five-ring banana-shaped mesogens with fluorine in the outer rings by Nguyen *et al.*[46] In both compounds (**8b**, **8c**) the four mesophases could be clearly distinguished by calorimetry. Since the textures are paramorphic it is difficult to recognise the phase transitions by polarising microscopy.

From preliminary electro-optical investigations on compound **8b** it follows that all mesophases show antiferroelectric switching although the threshold voltage is significantly increased below 131 °C. The spontaneous polarisation was found to be in the order of magnitude of 1000 $\mathrm{nC\,cm^{-2}}$, this value is comparable with that of the C_{PA} phase.

The three high-temperature phases described as $B_{2'}$, $B_{2''}$, $B_{2'''}$ display quite similar X-ray patterns which point to a B_2-like smectic phase. In the low temperature phase designated as B_X the outer diffuse scattering splits off and additional weak reflections appear in the middle angle region. X-Ray studies on oriented samples as well as NMR measurements are necessary to obtain more information about the structural features of these mesophases.

Selected topics

Are helical domains a sufficient criterion for a B_7 phase? (compounds 2c, 2d, 2g, 5g, 8f). Compounds **2c** and **2g** have already been described by Lee *et al.*[43,44] They found that the high temperature phase forms spontaneously left- and right-handed helical domains upon cooling the isotropic liquid. They designated this phase as B_7 since similar screw-like domains were also reported for the B_7 phase of nitro-substituted banana-shaped compounds.[10] We have reinvestigated compounds **2c** and **2g** by X-ray and by electro-optical measurements. For the mesophase of both compounds we found a simple layer structure. This finding is compatible with a B_2 phase but not with a B_7 phase which exhibits several incommensurate small-angle reflections in the X-ray diagram of a powder-like sample.[10] Furthermore, according to our electro-optical measurements the mesophase of compound **2c** shows antiferroelectric switching like a B_2 phase while for the mesophase of compound **2g** a very weak switching effect could be observed only near the clearing temperature. Compound **2g** behaves similarly to compound **2d** (the higher homologue of compound **2c**) which also forms helical domains but no noticeable switching could be observed. The mesophases of compounds **5g** and **8f** are comparable with that of compound **2c**. For example, Fig. 3 shows the growth of spiral germs and beaded filaments on slowly cooling the isotropic phase of compound **8f**. This picture is reminiscent of the nucleation of a B_7 phase. But the X-ray pattern of a powder-like sample displays only a Bragg and higher order reflections (see Fig. 4) indicating a simple layer structure, so a B_7 phase can be excluded. On the other hand, the switching behaviour is characteristic for a B_2 phase. As seen from Fig. 5 two current peaks per half period of an applied triangular voltage could be recorded which clearly points to an antiferroelectric ground state.

In this context it should be noted that the decyloxy homologue, described by Heppke *et al.*[42] with a chain length between **2c** and **2d**, possesses a mesophase which forms spiral domains and shows a pronounced antiferroelectric switching. Furthermore, it should be added that the smectic phase of

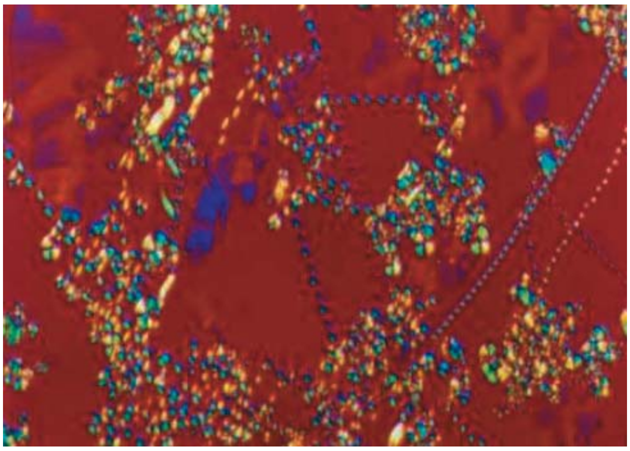


Fig. 3 Growth of spiral nuclei and beaded filaments of the B_2 phase of compound **8f** on cooling the isotropic liquid.

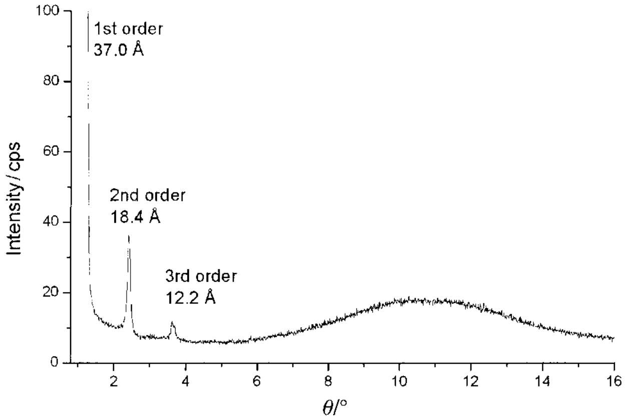


Fig. 4 X-Ray pattern of the B_2 phase of compound **8f** (128 °C).

terminally alkylthio-substituted banana-shaped mesogens reported by Heppke *et al.*[21] behaves similarly to compounds **2c**, **5g** and **8f**.

These results lead to the conclusion that the occurrence of helical nuclei is not sufficient to assign a mesophase as a B_7 phase. An essential criterion of a B_7 phase is the characteristic X-ray diagram (see Fig. 2). Another question is whether the switchable mesophases of compounds **2c** and **8f**, which form screw-like domains on cooling the isotropic liquid, are actually B_2 phases or they represent a new phase type. It is also still not clear why the mesophases of these compounds (**2c**, **5g**, **8f**) show antiferroelectric switching while the mesophases of compounds **2d** and **2g** do not show a noticeable switching effect. Further investigations, like X-ray studies and electro-optical measurements, are necessary to classify these phases.

The new sequence N–B_2 (compound 5e). The nematic phase of this compound **5e** exhibits a characteristic marbled texture (Fig. 6), but a homeotropic texture could never be obtained. At 97 °C the nematic phase is transformed into the B_2 phase which forms a non-specific grainy texture (Fig. 7). It is remarkable that the transition enthalpy from nematic to isotropic is rather low (0.85 kJ mol^{-1}) in comparison with the transition enthalpy B_2–nematic (9.1 kJ mol^{-1}).

The X-ray pattern of a powder-like sample of the B_2 phase shows a strong Bragg reflection in the small-angle region and its second order which is characteristic for a smectic layer structure. Otherwise, the diffuse scattering maxima in the wide angle region (10°) indicates a liquid-like order within the smectic layers. This diffuse scattering has a maximum at $d = 0.43$ nm corresponding to a transversal correlation length of about 1.4 nm. From the small-angle reflections a layer spacing of 3.5 nm can be derived and this remains constant in the whole range of existence of the B_2 phase.

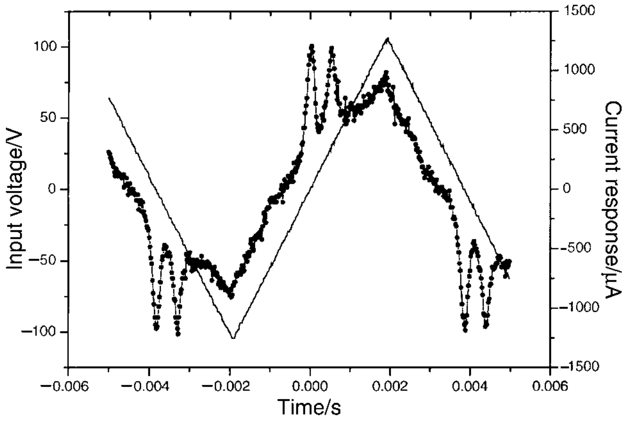


Fig. 5 Switching current response in the B_2 phase of compound **8f** obtained by applying a triangular voltage (±100 V; sample thickness 10 μm).

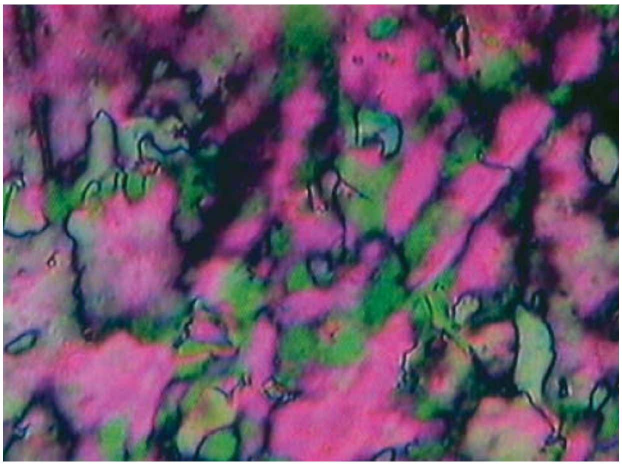


Fig. 6 Marbled texture of the nematic phase of compound **5e**.

Fig. 8 displays the X-ray patterns of an oriented sample. The orientation was achieved by the surface alignment on a glass plate. It can be seen in Fig. 8a that the molecules are aligned parallel to the glass plate. The diffuse scattering on the meridian corresponds to the lateral distance of the molecules. The maximum of the diffuse scattering in the small-angle region (not clearly seen in the presented pattern) yields an averaged period (only in the short range order) of 4.1 nm. Cooling down the sample into the B_2 phase (Fig. 8b) the sample is reorganised. The layer-normal is now parallel to the normal of the glass plate (equal to the meridian of the pattern) and the molecules are tilted with respect to the normal.

The tilt angle (35°) obtained from the fit of the outer diffuse scattering was found to be independent of the temperature.

In principle, the results of the X-ray investigations are also compatible with a SmC phase but the results of the electro-optical measurements unambiguously point to a B_2 phase. On applying a sufficiently high electric field the grainy texture transforms into a fan-like texture which exhibit irregular stripes parallel to the smectic layers. There are cases where the textures of the switched states are different for an opposite sign of the applied field indicating a "homochiral" ground state. But in most cases the textures of the switched state are independent of the polarity of the field corresponding to a "racemic" ground state. The current response to a triangular voltage shows two peaks per half period indicating an antiferroelectric switching behaviour. The spontaneous polarization was found to be 240 nC cm^{-2}; it does not markedly change with temperature (Fig. 9).

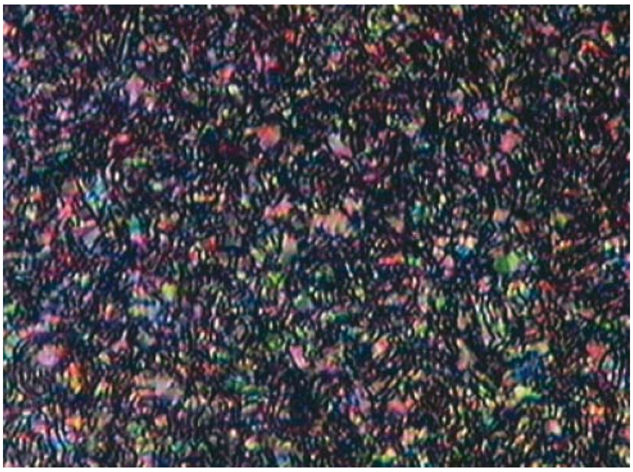


Fig. 7 Unspecific "grainy" texture of the B_2 phase of compound **5e**.

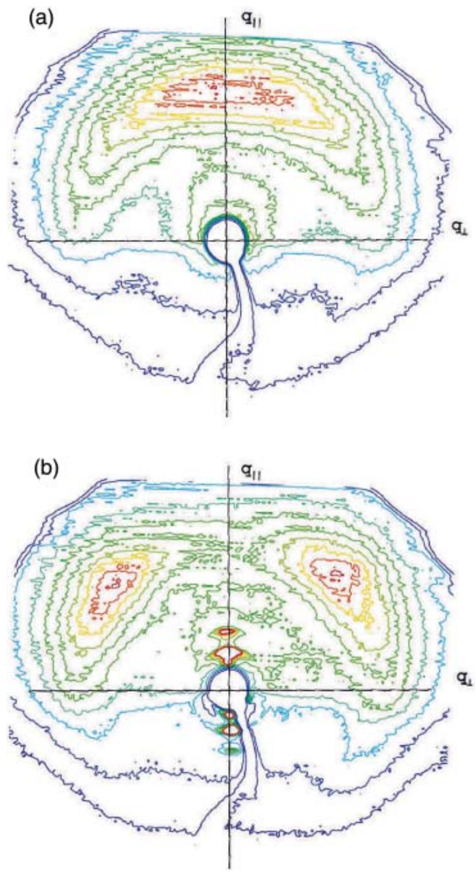


Fig. 8 X-Ray pattern of an oriented samples of compound **5e** a) nematic phase b) B_2 phase.

The first compound exhibiting the C_{PA} phase (compound 7c). Compound **7c** exhibits besides a SmA phase an additional smectic phase with an orthogonal alignment of the molecules and without in-plane order. But this smectic phase is a biaxial one and shows an antiferroelectric switching which is the result of a polar packing of the bent molecules in bent direction (similar to B_2 phases) whereby the direction of the polar axis alternates from layer to layer. A schematic picture is given in Fig. 10. From the analysis of the current response it follows that the spontaneous polarisation is about 1000 nC cm^{-2}. The existence of such a mesophase was theoretically predicted by Brand *et al.*[57] It was designated as C_{PA} where P refers to polar and A to antiferroelectric. Details concerning the experimental proof of this new smectic phase will be published elsewhere.

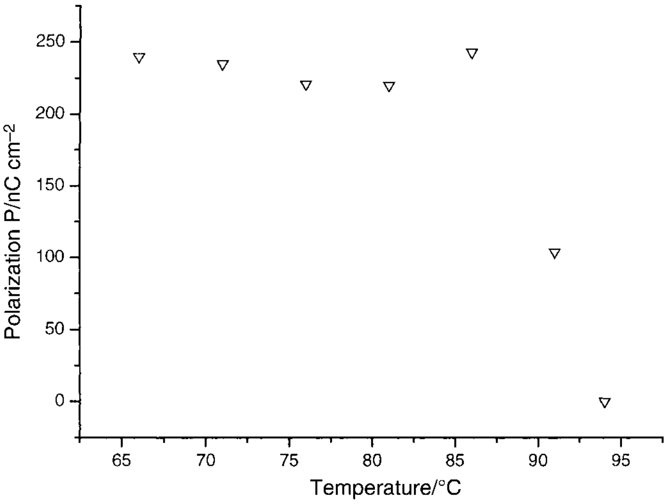


Fig. 9 Spontaneous polarisation of the B_2 phase of compound **5e** with temperature.

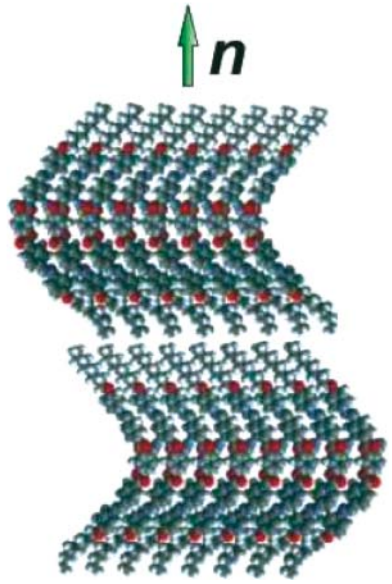


Fig. 10 Schematic picture of the C_{PA} phase.

The influence of fluorine substituents on the dielectric properties (compounds 2c, 8a, and 8b). As mentioned before the B_2 phase of compounds **8b** shows an unusually high value of the spontaneous polarisation of about 1000 nC cm^{-2}. This is obviously the result of three lateral fluorine substituents which are attached at the top of the central core as well as at the positions A of the terminal rings. For compound **8a** which has only a fluorine substituent at the central core the spontaneous polarisation is clearly reduced (670 nC cm^{-2}). The lowest value (370 nC cm^{-2}) was found for compound **2c**, where fluorine is substituted at the terminal rings, only. That means that the spontaneous polarisation of compound **8b** is about the sum of the corresponding values of compounds **8a** and **2c**. Dielectric measurements were carried out in order to find a correlation between the fluorine substituents, dielectric properties and the spontaneous polarisation.

From dielectric data in the frequency range from 10^{-3} to 10^{7} Hz information about the dynamics of polar groups as well as that of collective motions can be obtained. This measurement can also give an answer to the question which part of the molecule is responsible for the effect of fluorine substituents. For this reason the compounds **2c**, **8a** and **8b** were investigated. These samples could not be oriented in magnetic or electric fields. The measured relative permittivities ε' and the loss ε'' were fitted together as the complex dielectric permittivity $\varepsilon^{*}=\varepsilon'-j\varepsilon''$ to two Cole–Cole-absorption mechanisms (terms 1–3 of eqn. (1))

$$\varepsilon^{*}=\varepsilon_2+\frac{\varepsilon_0-\varepsilon_1}{1+(j\omega\tau_1)^{1-\alpha_1}}+\frac{\varepsilon_1-\varepsilon_2}{1+(j\omega\tau_2)^{1-\alpha_2}}-\frac{jA}{f}+\frac{B}{f^{N}} \quad (1)$$

with ε_i as low and high frequency limits, $\omega=2\pi f$ (f= frequency), τ_i = relaxation times, α_i = Cole–Cole distribution parameters, the conductivity terms 4 and 5 take into account the capacitance of the double layer.

The so obtained limits of the relative permittivities ε_i are presented in Figs. 11 to 13. An intensive low frequency mechanism, which exhibits a static relative permittivity ε_0 of about 40, could be separated in the kHz-region. As a result of this first relaxation process ε' decreases to $\varepsilon_1=10$. This mechanism could not be observed in the isotropic phase. The process responsible for this absorption is related to the

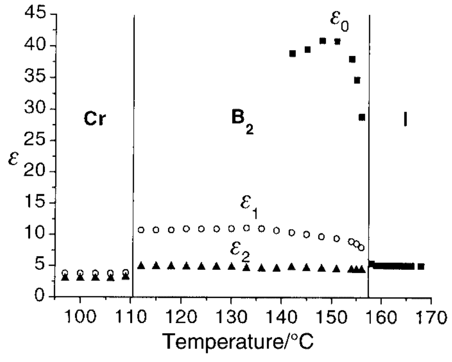


Fig. 11 Limits of the relative permittivity of compound **2c**.

collective dynamics of the antiferroelectric ordered dipoles in different layers. This relaxation could be clearly separated from the increase of capacitance due to the electrical double layer (term 5) for **2c** only above 140 °C.

For the following considerations only the high frequency mechanism is of interest. This is related to the reorientation of the perpendicular dipoles about the long molecular axes[31] and reduces the relative permittivity of **2c** from $\varepsilon_1 = 10$ to $\varepsilon_2 = 6$ ($\varepsilon_1 - \varepsilon_2 = 4$). It has already been demonstrated that this process shows a much lower intensity in the isotropic phase.[58] This is the reason why this relaxation is discussed as a mechanism with a strong positive dipole correlation which arises from the ferroelectric short range order. Thus, it is a direct measure for the co-operativity in the phase and should be related to the spontaneous polarisation.

For the sample containing the fluorine in the central position (see Fig. 12, **8a**) the increments $\varepsilon_1 - \varepsilon_2 = 36$ were calculated. The central and terminal fluorinated sample **8b** exhibits a higher intensity of the high frequency absorption mechanism of $\varepsilon_1 - \varepsilon_2 = 25$. Compounds **8a** and **8b** containing the fluorine in the central position show practically the same high increments. This underlines the importance of the central fluorinated samples and points to the influence of the central part of the molecule on the formation of the ferroelectric short range order and specially of the polar fluorine substitution as amplifier of the ferroelectric response. The relative permittivities of all three samples in the isotropic phase are about 5 pointing to the fact that the differences in the relative permittivites observed are mainly related to collective effects.

In the first approximation the dielectric increment $\varepsilon_1 - \varepsilon_2$ which is an indicator of the positive dipole correlation can be related to the spontaneous polarisation of the fluorine substituted compounds under discussion.

Discussion

We have carried out several investigations which illustrate the great influence of substituents at the central core of banana-shaped compounds on the mesophase behaviour. It was demonstrated that the kind as well as the position of the substituents are very important.[3] Some investigations were devoted to the influence of substituents at the terminal rings. In general it seems that this influence is less pronounced although in some cases new mesophases were described which have not been classified so far.

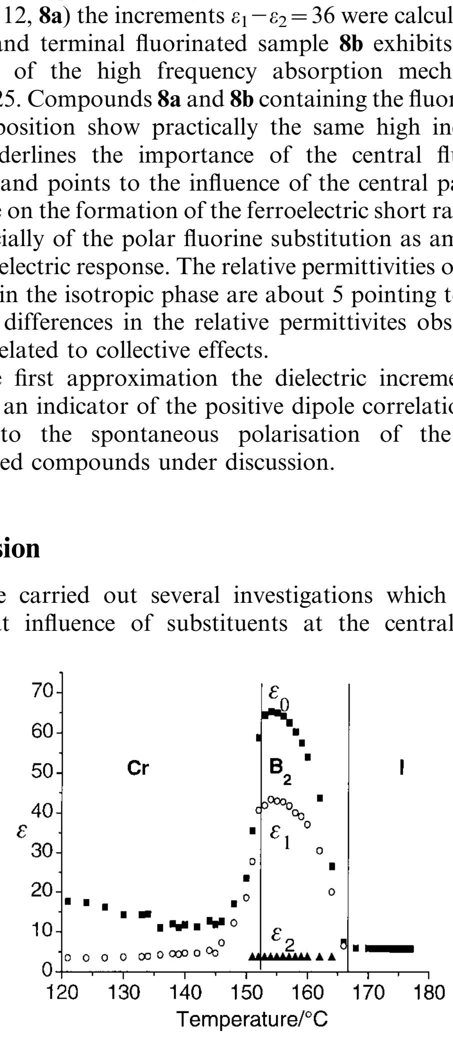


Fig. 12 Limits of the relative permittivity of compound **8a**.

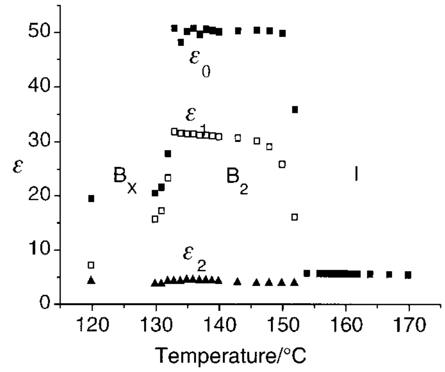


Fig. 13 Limits of the relative permittivity of compound **8b**.

In this paper we studied the mesophase behaviour of bent-shaped five-ring resorcinol derivatives which are not only substituted at the central core but also at the terminal rings. By a systematic synthetic design we were able to compare the mesophase behaviour of analogous compounds which possess the same substituents at the central core (and the same length of the terminal chains) but which are substituted at the terminal rings by different substituents in different positions.

Summarising the results it is obvious that the influence of the substituents at the central core is dominant. This is not surprising since substituents attached at the central phenyl ring near to the connecting groups can strongly influence the bending angle between the legs and therefore the conformation of the whole molecule. Optimal bending angles have been found to be between 110–140°.

The substituents at the terminal rings reduce the mesophase stability in comparison with corresponding non-substituted compounds. This effect is clearly greater for substituents in position B where in some cases mesophases can be completely suppressed. Furthermore, new phase sequences can be generated by the different positions of the substituents. With halogen substituents (F, Cl) in position A of the terminal rings the mesophase behaviour can be significantly modified. Introduction of fluorine in position A of the dodecyloxy homologue of the 4-chlororesorcinol series gives rise to the dimorphism B_2–SmA (compound **5d**) whereas the corresponding non-substituted compound **5a** forms a smectic A phase, only. The analogous octyloxy homologue derived from 4-chlororesorcinol substituted by fluorine in position B exhibits the new dimorphism B_2–N.

Other remarkable cases are derivatives of 5-fluororesorcinol which are substituted by fluorine atoms in the positions A. These compounds show mesomorphic tetramorphism. Although the structure of these phases is not known in detail they can be clearly assigned to B phases, since all four phases show antiferroelectric switching.

Another example of the effect of lateral substituents are 4,6-dichlororesorcinol derivatives where the attachment of fluorine or chlorine at position A can lead to the interesting phase sequences B_2–SmC–SmA (compound **6d**) or B_2–SmC–SmA–N (compound **6g**) in contrast to the compounds without substituents at the terminal rings which behave like calamitic compounds and do not form B phases.

It is interesting that the effect of substituents also depends on the length of the terminal chains. A well-known tendency which is also observed for other homologous series is seen by comparison of the homologous compounds **4e** and **4f**, where the short-chained octyloxy member forms a B_1 phase whereas the dodecyloxy derivative forms a B_2 phase.

Further interesting compounds are the 4-chlororesorcinol derivatives. The short-chained homologue substituted by fluorine in position A generates a B_2 phase (compound **5c**) whereas the dodecyloxy homologue **5d** shows the dimorphism B_2–SmA. If fluorine is introduced in the B-position the octyloxy derivative (compound **5e**) exhibits B_2–N dimorphism and the dodecyloxy homologue (compound **5f**) forms a B_2 phase only.

Among the 4,6-dichlororesorcinol derivatives which are substituted by fluorine in the A position the octyloxy homologue (compound **6c**) shows a SmA phase whereas the dodecyloxy derivative (compound **6d**) possesses the phase sequence B_2–SmC–SmA.

A last example should demonstrate the importance of the length of the terminal chains. In the case of 4-cyanoresorcinol derivatives where fluorine is introduced in position A the dodecyloxy compound **7d** shows mesomorphic trimorphism B_2–SmC–SmA whereas the octyloxy compound **7c** forms a smectic A phase together with a C_{PA} phase where the polar packed molecules are orthogonally ordered within the smectic layers.

These few examples clearly underline the importance of the terminal aliphatic chains; this is much more pronounced than in calamitic compounds. Therefore, in homologous series a great diversity of polymorphism including "banana"-phases and conventional phases can be expected.

Experimental

The structure of the products and intermediates was proved by ^{1}H NMR spectroscopy (Varian Gemini 200 and Varian Unity 400), mass spectroscopy (Intectra GmbH, AMD 402, electron impact, 70 eV), Finnigan MAT LCQ spectrometer and IR spectrometer Bruker IFS 66. Microanalyses were performed using a CHNS-932 (Leco Co.) elemental analyser.

The phase transition temperatures were determined with a differential scanning calorimetry (Pyris 1, Perkin Elmer) and a polarising microscope (Leitz Orthoplan) equipped with a Linkam THM 600 hot stage. The assignment of the mesophases is mainly based on X-ray diffraction measurements. X-Ray investigations on non-oriented samples were performed using Guinier goniometer or a Guinier film camera. X-Ray measurements on oriented samples were carried out with a 2D detector (HI-Star, Siemens AG). Electro-optical measurements were made using the usual experimental set-up described in an earlier paper.[31]

Dielectric measurements were carried out using a micro-capacitor ($d = 0.050$ mm, $A = 1$ cm^2) and the frequency range from 10^{-3} Hz to 10 MHz was covered using the Solatron Schlumberger Impedance Analyser.

Synthesis of substituted 4-(4-*n*-alkyloxyphenyliminomethyl)benzoic acids 1a–i

4-Formylbenzoic acid (50 mmol) was dissolved in 50 ml ethanol. 50 mmol of the corresponding substituted aniline were added and the mixture was refluxed for 8 hours. After cooling the product precipitated was filtered off and recrystallised twice from ethanol. Yields 54–76%. The phase transition temperatures are summarised in Table 1.

The analytical data are given for the 4-(3-fluoro-4-*n*-octyloxyphenyliminomethyl)benzoic acid **1c**. ^{1}H NMR (400 MHz, DMSO) $\delta = 0.82$–0.85 (m, 3H, CH$_3$), 1.23–1.40 (m, 10H, (CH$_2$)$_5$), 1.70–1.74 (m, 2H, OCH$_2$CH_2), 4.05 (t, $^3J = 6.6$ Hz, 2H, OCH$_2$), 6.26 (d, $^3J = 10.0$ Hz, 1H, Ar–H), 7.17 (d, $^4J = 2.4$ Hz, 1H, Ar–H), 7.33 (dd, $^3J = 10.0$ Hz, $^4J = 2.4$ Hz, 1H, Ar–H), 7.99 (d, $^3J = 2.0$ Hz, 2H, Ar–H), 8.01 (d, $^3J = 2.0$ Hz, 2H, Ar–H), 8.74 (s, 1H, CH=N), 10.09 (s, 1H, COOH). Elemental analysis for $C_{22}H_{26}O_3NF$ (371.45): calcd: C 71.07, H 7.06, N 3.77; found: C 71.05, H 7.41, N 3.32%. EIMS *m*/*z*: 371 (M$^+$). IR (Nujol) ν (cm^{-1}): 1680.5 (C=O), 1376.5 (C=N), 1107.0 (Ar–F).

Synthesis of substituted 1,3-phenylene bis(phenyliminomethyl)benzoates 2-8

2 mmol of the substituted resorcinol and 4 mmol of the corresponding substituted 4-(4-*n*-alkyloxyphenyliminomethyl)-benzoic acid were dissolved in 100 ml absolute dichloromethane. Dicyclohexylcarbodiimide (5 mmol) and a small amount of dimethylaminopyridine as catalyst were added. The mixture was stirred at room temperature for 48 hours. The solution was filtered off and the solvent was evaporated. The products were recrystallised manyfold from ethanol–dimethylformamide, and finally, from toluene–heptane. Yields 39–57%. The phase transition temperatures are listed in the Tables 2–8.

The analytical data are given for 1,3-phenylene bis[4-(3-fluoro-4-*n*-octyloxyphenyliminomethyl)benzoate] **2c**. ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 0.86$–0.90 (m, 6H, CH$_3$), 1.24–1.51 (m, 20H, (CH$_2$)$_5$), 1.79–1.86 (m, 4H, OCH$_2$CH_2), 4.05 (t, $^3J = 6.6$ Hz, 4H, OCH$_2$), 6.98 (t, $^3J = 8.8$ Hz, 1H, Ar-H), 7.04–7.06 (m, $^3J = 8.8$ Hz, $^4J = 2.5$ Hz, 1H, Ar-H), 7.09 (d, $^4J = 2.5$ Hz, 1H, Ar-H), 7.18 (d, $^4J = 2.2$ Hz, 2H, Ar-H), 7.22 (dd, $^3J = 8.0$ Hz, $^4J = 2.2$ Hz, 2H, Ar-H), 7.48 (d, $^3J = 8.0$ Hz, 2H, Ar-H), 8.01 (d, $^3J = 8.4$ Hz, 4H, Ar-H), 8.27 (d, $^3J = 8.4$ Hz, 4H, Ar-H), 8.52 (s, 2H, CH=N). Elemental analysis for $C_{50}H_{54}O_6N_2F_2$ (816.99): calcd: C 73.51, H 6.66, N 3.43; found: C 73.68, H 7.04, N 3.04%. EIMS *m*/*z* 816 (M$^+$). IR ν (cm^{-1}) (Nujol) 1730.3 (ArCOOAr), 1376.9 (C=N), 1107.8 (Ar–F).

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