Chapter 3 Substituted resorcinol derivatives

In the first part of this chapter there is a description of the synthetic work led to substituted resorcinol (1,3-dihydroxybenzene) derivative bent-shaped molecules fluorinated on the outer rings in different positions. In the second part, there is a description of the mesophase behavior of these compounds. Additionally, the intermediate two-ring calamitic materials are introduced.

The electro-optical and X-ray measurements were made in the work team of Professor Gerhard Pelzl (Martin-Luther-University Halle-Wittenberg, Germany) on the following instruments:

- the electro-optical measurements were performed with the help of LEICA DMRXP polarizing microscope equipped with METTLER-TOLEDO FP900 heating stage (Switzerland).
- the X-ray measurements were made on Guinier goniometer (Huber Diffraktionstechnik GmbH, Cu-Kα line) and either with a camera or with a 2D detector (HI-Star, Siemens AG) recorded.

The dielectric measurements were carried out in the work team of Professor Horst Kresse (Martin-Luther-University Halle-Wittenberg, Germany): the samples were put into a two-plate condensator and the signals were recorded by Hewlett Packard (HP 4192) impedance analyzer.

The NMR investigations were performed in the work team of Professor Siegbert Grande (University Leipzig, Germany) on Bruker MSL 500 spectrometer.

3.1 Synthetic work

The resorcinol derivatives were synthesized according to the following strategy (Fig 3.1):

1. Nucleophilic substitution of the commercially available 2- or 3-fluoro-4-nitrophenol was done to obtain 4-n-alkyloxy-3-fluoronitrobenzene (1) and 4-n-alkyloxy-2-fluoro-nitrobenzene (2) (hereafter abbreviated as 2/3-fluro…). Mitsunobu reaction (n-alkanol/PPh₃/DEAD in tetrahydrofuran, room temperature) [82] produced higher yield in some cases than the considerably cheaper modified
Fig. 3.1 General scheme of the synthesis of resorcinol derivative bent-shaped compounds. $R=H$ (9, 10), $R^2=$ NO$_2$ (11, 12), CH$_3$ (13, 14), $R^4=$ CN (15, 16), Cl (17, 18), $R^4=R^6=Cl$ (19, 20), $R^3=F$ (21, 22).
Williamson etherification (n-alkylbromide/K₂CO₃/KI in acetone or DMF under reflux) [83]. The reaction after Mitsunobu takes shorter time (2 days vs. 1 week), but the purification is more time-consuming in this case (removing O=PPh₃ derived from PPh₃ requires column chromatography). The difference in yield is not significant if the Williamson etherification is carried out in DMF under reflux (61% in Mitsunobu reaction vs. 53% in Williamson reaction for 2-fluoro-4-n-octyloxy-nitrobenzene). Note that 2-fluoro-4-nitrophenol becomes 4-n-alkyloxy-3-fluoro-nitrobenzene and 3-fluoro-4-nitrophenol turns into 4-n-alkyloxy-2-fluoro-nitrobenzene.

2. Nitro group reduction was carried out with hydrogen in ethylacetate with Pd catalyst. The resulting compounds are 4-n-alkyloxy-3-fluoro-anilines (3) and 4-n-alkyloxy-2-fluoro-anilines (4).

3. The anilines were led into condensation reaction with 4-formylbenzoic acid in ethanol under reflux. The resulting Schiff bases – 4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl)benzoic acids (5) and 4-(4-n-alkyloxy-2-fluoro-phenyliminomethyl)benzoic acids (6) – exhibit mesomorphism.

4. 5-Fluoro-resorcinol (7a) and 5-chloro-resorcinol (7b) are not commercially available. They were prepared by cleavage of the corresponding 3,5-dimethoxyhalogenobenzenes with BBr₃ in dichloromethane (Fig. 3.2) [84, 85].

![Fig. 3.2 Synthesis of 5-halogenoresorcinol, X=F, Cl](image)

4-cyanoresorcinol was available in the laboratory of the work team. Partially deuterated resorcinol and 2-methylresorcinol were prepared in the laboratory of Katalin Fodor-Csorba (Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, Budapest, Hungary).
There were several attempts to synthesize 4-fluoro and 4,6-difluororesorcinols using Selectfluor as fluorinating agent [85]. Since the first attempt had not been successful, the reaction circumstances were changed. The proportion of the reagents, the solvent, the reaction time and temperature had been varied. GC-MS investigations pointed out that always mixture of mono-, di- and even trifluorinated resorcinols were obtained. Fluorination of 2-methylresorcinol with Selectfluor was not successful either.

Some attempted synthesis were done to get 2-cyanoresorcinol from 2,6-dihydroxy-benzaldehyde and 2,6-dihydroxybenzamide. Reddy et al. could obtain this substance from 2,6-dimethoxybenzonitrile under extreme reaction circumstances: they hydrolyzed the diether by borontribromide at high temperature [73].

5. Reaction between (substituted) resorcinols (resorcinol 8a, 2-nitroresorcinol 8b, 2-methylresorcinol 8c, 4-cyanoresorcinol 8d, 4-chlororesorcinol 8e, 4,6-dichlororesorcinol 8f) and the 4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl)benzoic acids (5) or the 4-(4-n-alkyloxy-2-fluoro-phenyliminomethyl)benzoic acids (6) in presence of N,N’-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) catalyst [87, 88] produced the bent-shaped compounds (9-23).
3.2 Two-ring substances

3.2.1 4-(4-n-Alkyloxy-3-fluoro-phenyliminomethyl)benzoic acids (5)

On the way to synthesize new bent-shaped compounds rod-like mesogens (5, 6) were prepared, too.

All mesogens exhibit SmC and a low-temperature SmX phase (Fig. 3.3). Preliminary X-ray studies point to a new higher ordered smectic phase. The transition temperatures marginally change with increasing chain length. The transition temperatures and transition enthalpy values are shown in Table 3.1. In Fig. 3.4 the tendency of decreasing transition temperatures is illustrated.

\[
\begin{align*}
\text{Sign.} & \quad n & \text{Cr} & \text{SmX} & \text{SmC} & \text{I} \\
5.1 & 8 & \cdot & 147 & \cdot & 181 & \cdot & 261 & \cdot \\
5.2 & 9 & \cdot & 133 & \cdot & 176 & \cdot & 255 & \cdot \\
5.3 & 10 & \cdot & 112 & \cdot & 175 & \cdot & 254 & \cdot \\
5.4 & 11 & \cdot & 116 & \cdot & 171 & \cdot & 251 & \cdot \\
5.5 & 12 & \cdot & 114 & \cdot & 169 & \cdot & 246 & \cdot \\
\end{align*}
\]

Table 3.1 Transition temperatures (°C) and transition enthalpy values [kJ/mol] of 4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl)benzoic acids (5.1-5.5)
Fig. 3.3 The low-temperature SmX phase of compound 5.2 at 124°C

Fig. 3.4 Phase behavior of 4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl)benzoic acids (5.1-5.5)

3.2.2 4-(4-n-Alkyl-oxy-2-fluoro-phenyliminomethyl)benzoic acids (6.1 and 6.2)

These compounds exhibit nematic and smectic C mesophases. The difference is minimal between the clearing points of the two homologues. The melting points significantly decrease with lengthening the terminal chains (Table 3.2).
Chapter 3 Substituted resorcinol derivatives

![Chemical structure image]

Table 3.2 Transition temperatures (°C) and transition enthalpy values [kJ/mol] of the 4-(4-n-alkyloxy-2-fluoro-phenyliminomethyl)benzoic acids (6.1 and 6.2)

<table>
<thead>
<tr>
<th>Sign.</th>
<th>n</th>
<th>Cr</th>
<th>SmC</th>
<th>N</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>8</td>
<td>• 192</td>
<td>• 239</td>
<td>• 253</td>
<td>•</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[16.3]</td>
<td>[3.6]</td>
<td>[6.3]</td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>12</td>
<td>• 165</td>
<td>• 237</td>
<td>-</td>
<td>•</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[15.3]</td>
<td>[16.2]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comparing the phase behavior of the non-fluorinated [40] and the fluorinated mesogens the following conclusions could be drawn (Table 3.3):

- the 4-(4-n-alkyloxy-phenyliminomethyl)benzoic acids as well as the 6.1 and 6.2 exhibit smectic C and/or nematic mesophases. Compounds 5.1-5.5 exhibit two smectic mesophases.
- fluorination slightly decreases the clearing points (8-20°C),
- melting points hardly change if fluorine is introduced into position 2 (6.1 and 6.2), while significantly decreased if the compound is fluorinated in position 3 (5.1-5.5).

Table 3.3 Comparison of fluorinated and non-fluorinated 4-(4-n-alkyloxy-phenyliminomethyl)benzoic acids

<table>
<thead>
<tr>
<th>Sign.</th>
<th>n</th>
<th>Phase behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>[40]</td>
<td>8</td>
<td>Cr 190 SmC 255 N 261 I</td>
</tr>
<tr>
<td>5.1</td>
<td>8</td>
<td>Cr 147 SmX 181 SmC 261 I</td>
</tr>
<tr>
<td>6.1</td>
<td>8</td>
<td>Cr 192 SmC 239 N 253 I</td>
</tr>
<tr>
<td>[40]</td>
<td>12</td>
<td>Cr 155 SmC 255 I</td>
</tr>
<tr>
<td>5.5</td>
<td>12</td>
<td>Cr 114 SmX 169 SmC 246 I</td>
</tr>
<tr>
<td>6.2</td>
<td>12</td>
<td>Cr 165 N 237 I</td>
</tr>
</tbody>
</table>
Introduction of fluoro-substituent next to the position of the terminal chain positively influence width of the phase range. Furthermore a new mesophase (SmX) appeared. Fluoro substitution next to the position of the azomethine connection does not remarkably effect on the transition temperatures and the phase behavior.
3.3 Bent-shaped compounds derived from resorcinol and substituted resorcinols

In this chapter resorcinol-derivative compounds substituted or non-substituted on the central ring and fluorinated on the outer rings will be described. The chapter is divided in sections according to the chemical structure of the central ring, the consequence of the discussion follows the position of the substitution on the central ring, e.g. the first section is about the non-substituted resorcinol derivatives, the second about the 2-nitroresorcinol derivative, the last section is about the 5-fluororesorcinol derivative banana compounds. You will find an account of several novelties concerning the phase behavior of these substances:

- the first mesogens (9) probably exhibit SmC₀ phase (Section 3.3.1),
- the first bent-shaped compounds (15) with biaxial SmA (SmAP or CₚA) phase (Section 3.3.4),
- some examples of exceptionally rich polymorphism of switchable banana mesophases (Section 3.3.3 polymorphic SmCP (13) and Section 3.3.7 polymorphic B₅ phases (21)),
- the first issue (18.1) about SmCP phase formed on cooling the nematic phase (Section 3.3.5).

3.3.1 Resorcinol derivatives without substitution on the central ring (9, 10)

3.3.1.1 1,3-Phenylene bis[4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl)benzoates] (9)

In this section liquid crystalline materials exhibiting B₄, SmCP and most probably SmC₀ phase will be introduced [20]. All mesophases were experimentally proved.

Phase behavior (DSC)

As it is shown in Table 3.4 three mesophases appear on cooling. The SmC₀ - SmCP transition is not detectable with DSC. The B₄ soft-crystalline phase appears on the first cooling, and does not crystallize in reasonably long time. The melting and clearing points hardly, the transition temperatures slightly decrease with the length of
the terminal chains (Fig. 3.5). The shorter the terminal chains the wider SmCP and shorter SmC\(_G\) phase ranges exist.

![Chemical structure of substituted resorcinol derivatives](image)

<table>
<thead>
<tr>
<th>Sign.</th>
<th>n</th>
<th>Cr</th>
<th>B(_4^a)</th>
<th>SmCP</th>
<th>SmC(_G)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>8</td>
<td>• 129 (• 98)</td>
<td>• 164*</td>
<td>• 166</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[40.6]</td>
<td>[26.0]</td>
<td>[20.5]</td>
<td></td>
</tr>
<tr>
<td>9.2</td>
<td>9</td>
<td>• 123 (• 101)</td>
<td>• 153*</td>
<td>• 163</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[39.8]</td>
<td>[32.7]</td>
<td>[20.7]</td>
<td></td>
</tr>
<tr>
<td>9.3</td>
<td>10</td>
<td>• 123 (• 99)</td>
<td>• 147*</td>
<td>• 163</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[44.7]</td>
<td>[29.2]</td>
<td>[23.1]</td>
<td></td>
</tr>
<tr>
<td>9.4</td>
<td>11</td>
<td>• 121 (• 98)</td>
<td>• 141*</td>
<td>• 162</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[44.5]</td>
<td>[38.6]</td>
<td>[22.3]</td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>12</td>
<td>• 120 (• 98)</td>
<td>• 132*</td>
<td>• 160</td>
<td>•</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[49.8]</td>
<td>[50.4]</td>
<td>[22.5]</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) the B\(_4\) phase can be supercooled up to room temperature, the inverse transition B\(_4\) \(\rightarrow\) SmCP takes place about 10-12°C above this temperature

* not detectable with DSC. \(^5\) [89], \(^\S\) [90]

Table 3.4 Transition temperature (°C) and enthalpy values [kJ/mol] of substances 9.1-9.5 according to the DSC measurements
**Chapter 3 Substituted resorcinol derivatives**

![Graph](image)

**Fig. 3.5** Transition temperatures vs. chain length for compounds 9.1-9.5

**X-ray studies**

<table>
<thead>
<tr>
<th>Sign.</th>
<th>Molecular length $L$ (Å)</th>
<th>Spacing $d$±0.5 (Å)</th>
<th>Tilt angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>45.3</td>
<td>38.5</td>
<td>31.3</td>
</tr>
<tr>
<td>9.2</td>
<td>47.5</td>
<td>40.5</td>
<td>31.4</td>
</tr>
<tr>
<td>9.3</td>
<td>49.5</td>
<td>41.8</td>
<td>32.5</td>
</tr>
<tr>
<td>9.4</td>
<td>51.6</td>
<td>43.5</td>
<td>32.6</td>
</tr>
<tr>
<td>9.5</td>
<td>54.4</td>
<td>45.5</td>
<td>33.2</td>
</tr>
</tbody>
</table>

**Table 3.5** Molecular lengths, temperature-independent layer spacings and tilt angles found in compounds 9.1-9.5

XRD measurements performed on powder sample produced the outcome as follows:
- the layer spacing $d$ is temperature independent, it does not change either during the SmCG-SmCP or during the SmCP-B$_4$ transition (Table 3.5),
- the layer spacing linearly depends on the length of the terminal chain,
- from the proportion of the layer spacing to the effective molecular length ($L$) the tilt of the molecules within the layer is estimated about 32°,
- the correlation length $\xi$ determined from the full width at half maximum of the small angle X-ray reflection is temperature independent in the Sm$_C^G$ phase, while it continuously increases at the transition to the SmCP phase and abruptly decreases at the SmCP-B$_4$ transition.

**XRD measurements on surface-oriented sample**

In the Sm$_C^G$ phase four reflections occur in the small angle region (Fig. 3.6). They originate from differently oriented domains where the smectic layers are parallel and perpendicular to the substrate surface. The longer chained homologues (9.5) prefer orienting perpendicular, while the short chain homologue (9.1) parallel to the substrate surface. For compound 9.2 the probability is equal for growing in both directions.

![Fig. 3.6 X-ray pattern of the surface oriented sample for compound 9.5](image)

The maxima in the wide-angle region have been found to be out of the equator, what means the molecules are tilted with respect to the layer normal. The estimated tilt angle about 33 degrees is in good agreement with the values obtained from the diffuse scattering measurements. The Sm$_C^G$ phase is a smectic phase without in-plane order formed by tilted molecules. Orientation completely disappears in the B$_4$ phase.
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Electro-optical investigations and texture observations

Cooling the sample quickly from the isotropic phase non-specific grainy texture appears, while at slow cooling rate colored and gray ribbon-like growing domains as well as screw-like and telephone-wire filaments have been observed (Fig. 3.7).

![Image](image.png)

**Fig. 3.7** Formation of SmC\(_G\) phase on cooling the compound 9.2

When the growing domains are surrounded with isotropic liquids application of electric field affects on the texture. Depending on the polarity of the field the grey ribbons grow or shrink. Exposing the ribbons to an electric field they coil into spirals formed clockwise or anticlockwise depending on the polarity of the field. The behavior of the ribbons in electric field tallies with the observations given by A. Jákli et al. in favor of SmC\(_G\) phase [29]. The screw-like filaments coil, moreover grow as flat nuclei in case of long-time exposure even grow as flat nuclei in electric field (Fig. 3.8). When the texture covers the whole view-field of the microscope electric field does not markedly effect on the texture. On further cooling the fan-shaped texture changes into a grainy one, it indicates a phase transition. In this low-temperature phase the field-induced texture is independent from the polarity of the field.

On cooling the SmC\(_G\) phase the chiral domains remain unchanged at the transition into the SmCP and B\(_4\) phases. In the B\(_4\) phase the texture shows nearly extinction between the crossed polarizers and the contrast between the domains of opposite handedness is less pronounced. These domains neither change upon a reversed transition on
heating from the B4 phase. Only the formation of the SmCP phase from the B4 phase is delayed, taking place at about 10 degrees higher temperature. Similar hysteresis behavior will be reported in chapter 5 [91].

Fig. 3.8 Microscopic texture of SmCP phase of the compound 9.3 at 133°C a) E=0 Vµm⁻¹ b) E= ±20Vµm⁻¹

Depending on the experimental conditions (cooling rate; surface treatment) different behavior have been observed. During the nucleation of the SmCG phase one-dimensionally growing screw-like domains as well as large chiral domains grow simultaneously (Fig. 3.9). The screw-like domains further transform into a grainy texture, whereas the large chiral domains remain unchanged.

The high temperature SmCG phase is not switchable: the strong sterical hindrance inhibits turning of the leaning molecules in the smectic plane. The low temperature phase is an antiferroelectric mesophase with synclinic symmetry, i.e. SmC₅Pₐ mesophase. Unexpectedly, the spontaneous polarization shows pronounced odd-even effect in spite of the long terminal chains.

As it has already been mentioned in section 2.2 the molecules in the SmCP phase can adjust four kinds of structures: AFE anticlinic and synclinic (SmC₅Pₐ, SmC₅Pₐ), FE anticlinic and synclinic (SmC₅Pₐ, SmC₅Pₐ) [25, 92]. The two states AFE and FE are separated by a small energy barrier. In most instances the energy of the AFE state is somewhat lower than one of the FE state resulting in the AFE ground state either synclinic or anticlinic. Application of an electric field leads to the transition from the AFE into FE state. The chirality of the layers is mainly conserved (observed transitions are SmC₅Pₐ → SmC₅Pₐ and SmC₅Pₐ → SmC₅Pₐ). Recent Fourier transform infrared
spectroscopic measurements also indicated a motion of the long molecular axis on the cone as in the SmC* phase [93].

A detailed investigation of the switching in the SmCP phase is reported in the ref. [94]. They observed that the appearance of the synclinic or anticlinic ground state can also be influenced by the shape of the oscillating external field. However, the SmC₅P₅ ground state has lower energy. Dielectric spectroscopy measurements separately performed on racemic and homochiral samples showed quite different properties of the domains. In the racemic state the switching is about twice as fast as in chiral state. The dielectric strength $\Delta \varepsilon$, however, is about twice as high in the chiral state. Further analysis of the effects of the chiral and racemic domains in the SmCP phase has been reported by L.M. Blinov et al. [95] on the base of the analysis of the fine structure of the current response peaks.

### 3.3.1.2 1,3-Phenylene bis[4-(4-alkyloxy-2-fluoro-phenyliminomethyl)benzoates] (10.1 and 10.2)

These compounds exhibit switchable SmCP mesophase. Since there is a tiny change in the clearing point and a slight decrease in the melting point with chain-
lengthening the mesophase range is wider in the dodecyloxy (10.2) homologue (Table 3.6).

[Chemical structure image]

<table>
<thead>
<tr>
<th>Sign.</th>
<th>n</th>
<th>Cr</th>
<th>SmCP</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1</td>
<td>8</td>
<td>•</td>
<td>127</td>
<td>•</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>10.2</td>
<td>12</td>
<td>•</td>
<td>117</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[42.6]</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6 Transition temperature (°C) and enthalpy values [kJ/mol] of compounds 10.1 and 10.2 according to the DSC measurements

The mesophase appears with Schlieren and non-specific grainy texture. At the freezing point this texture freezes and becomes glassy. NMR measurements pointed out that in 10.1 the bending angle between the two wings is about 118-120 deg, what means that the molecule is really bent. The order parameter $S$ is around 0.82 corresponding to $S$ values found in banana mesophases in earlier studies [2].

Comparing the phase behavior of fluorinated (9.1-9.5, 10.1 and 10.2) and non-fluorinated* [1, 33] resorcinol derivatives:

- fluorination decreases the melting points, in case of compounds 9.1-9.5 they are slightly changed, whilst in 10.1 and 10.2 there is a significant difference between them,
- the clearing points change similarly to the melting points,
- all three kinds of bananas exhibit enantiotropic SmCP mesophase. The mesophase range is wider in the fluorinated substances.
- a new mesophase SmC$_G$ appears in 9.1-9.5,
• in 10.1 and 10.2 crystalline banana phases (B₃, B₄) disappear.

* The non-fluorinated substances, 1,3-phenylene bis[4-(4-n-alkyloxynylaminomethyl)benzoates] display the following phase behavior [1, 33]: if n=8 B₄ 139 B₃ 152 B₂ 174 I and if n=12 B₄ 141 B₂ 170 I.
3.3.2 2-Nitroresorcinol derivatives (11, 12)

All fluorinated bananas derived from 2-nitroresorcinol derivatives exhibit the exotic B₇ mesophase [61] (Table 3.7) as well as the non-fluorinated compounds [30]. This phase appears with two-dimensional patterns indicating a helical superstructure. However, neither substance could be oriented, therefore detailed characterization of B₇ phase is one of the most challenging tasks of the future.

Dielectric measurements point to a crystalline-like monotropic low-temperature phase in compound 11.1 [96]. The mesophase B₇ does not crystallize anymore after the first heating of 11.1.

![Chemical structure of 2-nitroresorcinol derivatives](image)

<table>
<thead>
<tr>
<th>Sign.</th>
<th>X</th>
<th>Y</th>
<th>n</th>
<th>Cr</th>
<th>Bₓ</th>
<th>B₇</th>
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<td>H</td>
<td>8</td>
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<td>81</td>
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</tbody>
</table>

* for compound 11.1 data are given on cooling

# this transition is not detectable on DSC

Table 3.7 Transition temperature (°C) and enthalpy values [kJ/mol] according to the DSC measurements
Chapter 3 Substituted resorcinol derivatives

Comparison of compounds 11 and 12 and non-fluorinated 2-nitroresorcinol derivatives* [30] points to the following conclusions:

- all compounds exhibit B7 mesophase,
- the melting point decreases by about 60°C if fluoro-substituent is introduced in position 3, while fluoro-substitution in position 2 hardly changes it,
- the clearing point decreases by about 10°C in 11.1 and 11.2, and 20°C in 12.1 and 12.2. Since characterization of B7 phase is in an early state compounds with sunk transition temperatures might be good candidates for extensive studies.
- dielectric measurements suggest that the octyloxy homologue of the non-fluorinated substance and 11.1 have a low temperature B_\text{x} phase.

* The non-fluorinated mesogens, 2-nitro-1,3-phenylene bis[4-(4-n-alkyloxyphenyliminomethyl) benzo- ates] have the following phase behavior [30]: n=8 X=Y=H Cr 87 B_\text{X} 129 B_7 177 I and if n=12 X=Y=H Cr 85 B_7 173 I.
3.3.3 2-Methylresorcinol derivatives

3.3.3.1 2-Methyl-1,3-phenylene bis[4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl)benzoates] (13)

In this section substances with polymorphic switchable banana mesophases (SmCP, B5, Bx) will be introduced. The octyloxy homologue (n=8) was thoroughly researched [56], even its deuterated analogue was synthesized to enable extensive NMR investigations never have been carried out before.

Phase behavior (DSC)

![Chemical structure of 2-Methyl-1,3-phenylene bis[4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl)benzoates] (13)]

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</table>

* this transition not seen on DSC
~ sum of $\Delta H$ at B2’-B2 and B2-B5 transitions

Table 3.8 Transition temperature (°C) and enthalpy values [kJ/mol] of 13.1-13.5 on cooling provided by DSC measurements
These substances exhibit very rich variety of mesophases. The long chain homologues were not fully investigated, so the phase assignment is a preliminary. Neither polarization microscopy nor DSC measurements can provide information about the $B_2'$-$B_2''$ transition of compound 14.1. At the same time the $B_2'$-$B_2''$ transition is detectable with both techniques. Therefore the existence of $B_2'$ mesophase in compounds 13.2-13.5 could be determined preliminary. The $B_x$ phase is not identical with the $B_x$ phase mentioned in section 3.3.2. As you can see on Fig. 3.10 the clearing point hardly, the melting point slightly decreases with increasing terminal chain length. The longer terminal chain the wider SmCP and $B_x$ and the narrower $B_5$ phase ranges were found.

Polarizing microscopy and electro-optical measurements

These observations were made on compound 13.1. The $B_2$ phase appears on cooling of the isotropic liquid exhibiting a grainy or fan-shaped texture (Fig. 3.11a). There is no texture change at the transitions $B_2 \rightarrow B_2'$, whereas at the transition $B_2' \rightarrow B_2''$ paramorphic smooth fan-shaped textures appears (Fig. 3.11b). There is a minor change in the texture at the transition into the $B_5$ phase: a small change of the birefringence and the formation of irregular stripes perpendicular to the fans have been ob-
served (Fig. 3.11c). The transition into the low-temperature phase B_X could not be seen by polarizing microscopy.

**Fig. 3.11** Optical textures of compound 13.1 at 148°C B_2 phase (a), 140°C B_2'' phase (b) and at 130°C B_5 phase (c)
All four phases showed similar electro-optical responses to the applied d.c. electric field. The initial fan-shaped texture transformed into a smooth SmA-like fan-shaped texture at the field higher than a threshold 0.5 - 0.8 V/μm for the mesophases B₂, B₂′, B₂″ and B₅ (Fig. 3.12 and 3.13). The textures relaxed into their initial state when the external field was removed (at \( E = 0 \)).

![Fig. 3.12](image1.png) Field induced texture change of the B₂′ phase at 143°C a) field-off state b) \( E = \pm 2.8 \) V/μm

![Fig. 3.13](image2.png) Field induced texture change of the B₅ phase at 132°C a) field-off state b) \( E = \pm 4.8 \) V/μm

The spontaneous polarization is temperature dependent, its maximum value is 800 nC/cm². At the transition into the low-temperature phase Bₓ the threshold significantly increases. The relaxation from the polarized state into the ground state is quite
slow, probably due to high viscosity of the sample; otherwise the switching behavior is quite similar to that of the B$_5$ phase.

X-ray measurements

The patterns of oriented samples provide important details about the mesophases. The high temperature phase exhibits a pattern without in-plane order, typical for SmCP: the layer reflections are observed on the meridian of the pattern; the maxima of the broad outer diffuse scattering are situated out of the equator indicating an inclination of the molecules and the absence of the long-range positional order within the layers. From the $\chi$-scan the tilt angle of about 25 deg has been derived. On cooling the sample into the B$_2^{\|}$ phase the meridian reflections reproducibly split up into pairs. This splitting corresponds to an angle ~ 6 deg between the layer normal and the fiber axis. This additional tilt is too small to be detected from the wide-angle diffuse outer scattering. However, this change conforms to alterations in the NMR spectra. The split peaks merge again on the meridian at the transition into the B$_2^{\|\|}$ phase at 142ºC. Below 135 ºC the scattering diagram shows formation of a two-dimensional rectangular cell within the layers on a short-range scale characteristic of B$_5$ phase [26]. The pattern of the B$_X$ phase indicates the positional correlation of the molecules in adjacent layers. The phase is assumed as a three-dimensional crystalline one with large amount of disorder. Furthermore an in-plane organization of the molecules described by an orthorhombic cell can be inferred. The pattern also hints at more complex structure could not have been proved yet. The next change of the X-ray pattern takes place below T $\cong$ 102 ºC to a true crystalline phase.

Dielectric measurements

The phase transition B$_2^{\|}$/B$_2^{\|\|}$ could be interpreted with the help of dielectric spectroscopy: the decrease of the parameters $\Delta_2$ and $\varepsilon_2$ at the B$_2^{\|}$/B$_2^{\|\|}$ transition may indicate that in the B$_2^{\|\|}$ phase the interaction of the dipoles is reduced with respect to that in the B$_2^{\|}$ phase. The detected high strength $\Delta_2$ is in the same order of magnitude as in case of B$_2$ modifications and indicates a strong positive dipole correlation in the B$_5$ as well as in
the B$_2$ phase. The decrease of $\Delta_2$ at the B$_5$/B$_X$ transition may be connected either with a complete disappearance or a stepwise decrease of the relaxation frequency of some decades (phase transition into a highly ordered solid-like B phase).

**NMR studies**

![Compound 13.1d: bent-core molecule deuterated on the central ring](image)

NMR measurements were made on the compound 13.1 and deuterated 13.1 (13.1d, see Fig. 3.13). There is no difference between the phase behavior of 13.1 and 13.1d. Partial substitution by deuterium enables finding both the longitudinal ($S$) and the transversal ($D$) order parameters. The order parameter $S$ in the high-temperature B$_2$ phase was obtained using both $^1$H-NMR and $^2$H-NMR techniques under the assumption that the molecules are oriented parallel to the magnetic field. Three regions can be distinguished in the temperature interval of the B$_2$-like phases (152 °C – 136 °C) (Fig. 3.14). The first interval between the clearing point and ~145 °C where the splitting is almost independent of the temperature, then the splitting experiences a jump and again a small plateau up to 142 °C. This region we designate as the B$_2$/ phase. The transition into the B$_2/$ phase is accompanied by a small latent heat detected on the DSC curve. The proton splitting is monotonically increasing with decreasing temperature and at 136 °C it reaches saturation upon the transition into the B$_5$ phase. The calculated value of $D$ in high-temperature range is very small: $D < 0.01$. Therefore at lower temperatures $D$ was assumed to be negligibly small, and only $S$ was calculated from the splitting of $^2$H.
Chapter 3 Substituted resorcinol derivatives

Fig. 3.14 Order parameter of compound 13.1d obtained from NMR measurements

The long-chain homologues (n=9-12) show similar phase behavior under polarizing microscope and according to the DSC studies as 13.1. XRD measurements are necessary to provide unambiguous information, though.

3.3.3.2 2-Methyl-1,3-phenylene bis[4-(4-n-alkyloxy-2-fluoro-phenyliminomethyl)benzoates] (14.1 and 14.2)

The compounds 14.1 and 14.2 were preliminary studied by polarizing microscopy and electro-optics. These substances have lost polymorphism owing to fluorination in position 2 on the outer rings. Fluorination in this position influenced the phase behavior so unfavorably that the short-chain homologue exhibits only a monotropic non-switchable B₁ mesophase. Terminal chain lengthening, as usual, led to the appearance of B₂ phase. However, B₂-B₅ polymorphism does not show up either.
Chapter 3 Substituted resorcinol derivatives

Comparing the non-fluorinated mesogens* [26] and 13.1-13.5 and 14.1, 14.2 the following points can be raised:

- fluorination considerably changes the phase behavior in the case of 2-methylresorcinol derivatives,
- the short-chain (n=8) homologue of the non-fluorinated compound exhibit B2 and B5, the dodecyloxy homologue B2 mesophases,
- in compounds 13.1-13.5 unique polymorphism of switchable mesophases appears,
- in compounds 14.1 and 14.2 only the dodecyloxy homologue exhibits switchable B2 mesophase,
- additionally, fluorination in both positions considerably decreases the melting points,
- the clearing points fall due to fluorination.

* The 2-methyl-1,3-phenylene bis[4-(4-n-alkyloxyphenyliminomethyl)benzoates], the non-fluorinated mesogens, have the following phase behavior [26]: if n=8 Cr 161 B5 165 B2 172 I and if n=12 Cr 148 B2 164 I.

Table 3.9 Transition temperature (°C) and enthalpy [kJ/mol] values of compounds 14.1 and 14.2

<table>
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3.3.4 4-Cyanoresorcinol derivatives

In this section you will read about materials exhibiting SmAP (C_{PA}) – an orthogonal, but switchable – mesophase. Brand et al. [16, 97] predicted this kind of phase behavior of bent-shaped mesogens. These are the first substances where the existence of SmAP was found and could be proved [22].

3.3.4.1 4-Cyano-1,3-phenylene bis[4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl) benzoates] (15)

These substances exhibit a high-temperature SmA and a low-temperature SmAP switchable mesophase. Both mesophases are enantiotropic and appear independently of the chain length.

![Chemical structure of 4-Cyano-1,3-phenylene bis[4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl) benzoates]](image)

<table>
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<th>SmA (°C)</th>
<th>I (°C)</th>
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<td>[18.2]</td>
<td>[0.7]</td>
<td>[8.1]</td>
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</table>

| Table 3.10 | Transition temperature (°C) and enthalpy [kJ/mol] values of compounds 15.1-15.5. |
As you can see in Fig. 3.15 the clearing and melting points marginally deviate from a value. The transition temperature of the phase transition SmAP-SmA slightly decreases with increasing chain length what means that the SmA phase range becomes wider with chain-lengthening, the change is not considerably, though. The compound 15.1 was investigated in details, and will be introduced in the following.

*Polarizing microscopy and electro-optical measurements*

Both mesophases can be observed by polarizing microscopy. SmA phase appears with fan-shaped or homeotropic texture as usual. The SmAP phase shows up with a subtle change in the fan-shaped texture: irregular fine stripes parallel to the smectic layers appear (Fig. 3.16). The homeotropic texture, at the same time, turns into a strongly fluctuating schlieren one. At further cooling the fluctuation in the schlieren texture disappears, in the meantime it becomes more birefringent.

The SmA phase is not switchable. Applying electric field to the fan-shaped texture of SmAP phase the stripes disappear. Meanwhile, the birefringence has been changing. At lower temperatures the switching becomes slower and happens within
seconds. The current response proves the antiferroelectric nature of this phase. The polarization is unusually high in the SmAP phase: its value reaches 1000 nCcm\(^{-2}\).

Fig. 3.16 Fan-shaped (a) and schlieren texture (b) of the SmAP phase

*X-ray measurements*

![X-ray measurements graph](image)

Fig. 3.17 Temperature dependence of the layer spacing \(d\) and the tilt angle \(\Theta\) [17]

The X-ray diffraction pattern exhibits an outer diffuse scattering, the maxima of which are clearly positioned on the equator, also in the phase below the SmA phase. No
change in the patterns appears down to 45 °C, where the layer reflections become more crescent-like and the outer diffuse scattering splits into a few peaks resulting from the appearance of an in-plane order. It is clearly seen that these wide-angle reflections still remain diffuse. The derived tilt angle obtained from the analysis of the diffuse outer scattering as well as the layer spacing versus temperature is illustrated in Fig. 3.17.

NMR measurements

Since the molecule is substituted in position 4 on the central ring, the long axis different from the symmetry axis of a non-substituted molecule. It could be proved from the anisotropic shift of the CN carbon that the deviation is around 5 degrees. The order parameter was derived from the shift anisotropy of the central ring protons and carbons. The dependence of the order parameter is shown in Fig. 3.18. The bending angle $\alpha$ was found to be around 142 degrees in the SmA, and 132 degrees in the SmAP phase.

Fig. 3.18 The temperature dependence of the order parameter in compound 15.1 [17]
3.3.4.2 4-Cyano-1,3-phenylene bis[4-(4-n-alkyloxy-2-fluoro-phenyliminomethyl) benzoates] (16)

These compounds exhibit high-temperature nematic and/or SmA and low-temperature SmCP mesophases. The mesophase behavior was observed only by polarizing microscopy. The grainy texture of the low-temperature phase gives a hint that it is a SmCP and not only a SmC phase. Preliminary electro-optical studies have shown that the low-temperature mesophase is switchable.

\[
\begin{align*}
\text{H}_2n+1\text{C}_n\text{O} & \quad \text{O} \\
\text{N} & \quad \text{C} \\
\text{F} & \quad \text{F} \\
\text{C}_n\text{H}_{2n+1} \quad \text{O} & \quad \text{C}
\end{align*}
\]

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<th>SmA</th>
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# not observable on DSC

Table 3.11 Transition temperature (°C) and enthalpy [kJ/mol] values of compounds 16.1 and 16.2

Comparing the non-fluorinated* [65] and both series of fluorinated 4-cyanoresorcinol derivatives (15.1–15.5, 16.1 and 16.2) the following conclusions can be drawn:

- the clearing point decreases in substances 16.1 and 16.2, does not change considerably in compounds 15.1-15.5,
- the difference between the melting points (m. p.) of the octyloxy and the dodecyloxy derivatives do not change more than 2°C in the case of the fluorinated
materials (15.1-15.5, 16.1, 16.2), while the m. p. of the non-fluorinated dodecyloxy derivative is 32°C below the m. p. of the short-chain (n=8) homologue,

- each compound exhibits SmA, 16.1 an additional nematic phase. It enhances the chance to orient the low-temperature SmCP phase in weak magnetic field.

- each compound exhibits switchable mesophase: in compounds 15.1-15.5 SmAP phase appears, whilst the other substances exhibit SmCP phase,

- the switchable mesophase range is very wide (45-73°C) except for the compounds 16.1 where it takes only 2°C and compound 16.2 where it is moderately wide (31°C),

- all in all fluorination on the outer ring in position 2 (16.1 and 16.2) unfavorably influences the phase behavior, while in position 3 (15.1-15.5) considerably changes the structure of the switchable mesophase. It converts tilted SmCP into orthogonal SmAP mesophase.

* The phase behavior of the 4-cyano-1,3-phenylene bis[4-(4-n-alkyloxyphenyliminomethyl)benzoates], the non-fluorinated compounds [65]: n=8 Cr 97 SmCP 142 SmC 146 SmA 175 I and if n=12 Cr 65 SmCP 122 SmC 141 SmA 188 I.
3.3.5 4-Chlororesorcinol derivatives

In this section you will read about compounds exhibiting SmCP (B₂) mesophase. There are few examples when this mesophase appears on cooling conventional smectic mesophases (SmC or SmA) [64]. Here you can find the first instance of SmCP emerging from nematic phase.

3.3.5.1 4-Chloro-1,3-phenylene bis[4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl) benzoates] (17)

Phase behavior (DSC)

The short-chain homologue 17.1 exhibit SmCP, the long-chain homologue (n=12) SmCP and an additional SmA high-temperature mesophase. It is a rare phenomenon that the long-chain homologue exhibits an additional less-ordered high-temperature mesophase. The melting point marginally decreases, the clearing point subtly increases with chain-lengthening. The SmCP phase exists in wide range, while the SmA phase has six-degree-temperature range. Electro-optical and XRD studies were carried out on the substance 17.1. The results will be introduced in the following.

![Chemical structure of 4-Chlororesorcinol derivatives](image)

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Table 3.12 Transition temperature (°C) and enthalpy [kJ/mol] values of compounds 17.1 and 17.2
On cooling the isotropic liquid, the SmCP phase appears with grainy fan-shaped texture. Applying electric field stripes parallel to the smectic layers appear. In this phase the field induced texture is independent of the polarity of the field. The switching polarization does not show any temperature dependence. Applying sufficiently high triangular voltage antiferroelectric switching could be observed (Fig. 3.19).

![Fig. 3.19 Current response of compound 17.1](image)

The X-ray pattern without in-plane order is typical of SmCP phase: the layer reflections are observed on the meridian of the pattern; the maxima of the broad outer diffuse scattering are situated out of the equator indicating an inclination of the molecules and the absence of the long-range positional order within the layers. From the $\chi$-scan the tilt angle of about 19 degrees has been derived.
3.3.5.2 4-Chloro-1,3-phenylene bis[4-(4-n-alkyloxy-2-fluoro-phenyliminomethyl)benzoates] (18)

*Phase behavior*

These compounds exhibit SmCP, the short-chain homologue (n=8) an additional nematic phase. The melting point decreases, the clearing point increases with chain lengthening. Compound 17.1 was investigated in details, and will be described in this section.

![Chemical structure of compound 18.1](image)

<table>
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</table>

*Table 3.13 Transition temperature (°C) and enthalpy [kJ/mol] values of compounds 18.1 and 18.2*

*Polarizing microscopy and electro-optical measurements*

The high-temperature nematic phase in the compound 18.1 exists in a short temperature interval of 4°C and shows characteristic schlieren or marble textures (Fig. 3.20). On cooling the schlieren texture transforms into a fine-grainy one. The compound 18.1 shows the electro-optical switching at high threshold field of about 100 V/μm. The switching polarization does not show any temperature dependence in the SmCP phase. The polarization value in SmCP mesophase is around 250 nCcm⁻².
Chapter 3 Substituted resorcinol derivatives

X-ray investigations

X-ray measurements on non-oriented samples showed the layer reflections up to the second order and broad diffuse scattering in the wide-angle region. The $d$-value is about 35 Å and temperature independent.

Experiments on oriented samples proved the existence of the SmCP phase as well as the high-temperature nematic phase. The splitting of the outer diffuse maxima indicates a tilted arrangement of the molecules in the smectic layers what is compatible with the SmCP phase. The splitting does not show any temperature dependence. In case of surface oriented samples the analysis of the wide-angle scattering shows a change of the molecular orientation upon the N→SmCP transition: the molecules lay parallel to the surface in the nematic phase, while the smectic layers are perpendicular to it in the smectic C phase. From the $\chi$-scan the tilt angle in SmCP phase is approximately 35 degrees, which is close to the value could be estimated from the layer spacing.

Comparison the non-fluorinated* [64] and both fluorinated 4-chlororesorcinol derivatives (17.1, 17.2, 18.1 and 18.2) has the following outcome:

- the clearing point decreases by 30°C only in case of compounds 18.1 and 18.2, fluorination in position 3 does not effect on the clearing point,
- fluorination significantly decreases the melting point: in 17.1 and 17.2 $\Delta T \sim 30^\circ$C, in 18.1 and 18.2 $\Delta T \sim 40^\circ$C,
• all substances exhibit SmCP mesophase, fluorination positively influences the width of the mesophase range,
• in compound 17.2 a high-temperature SmA, in compound 18.1 a nematic mesophase appears,
• altogether fluorination on the outer rings in any position positively influences the phase behavior of 4-chlororesorcinol derivatives: the temperature range of the switchable mesophase has become wider, and SmA-SmCP as well as N-SmCP polymorphism occur.

* The non-fluorinated substances, 4-chloro-1,3-phenylene bis[4-(4-alkyloxyphenyliminomethyl)benzoates] show the following mesophase behavior [64]: n=8 Cr 120 SmCP 133 I; n=12 Cr 115 SmCP 142 I.
3.3.6 4,6-Dichlororesorcinol derivatives

In this section you will read about bent-core mesogens with unusually wide bending angle between the wings. It results in rich polymorphism of mesophases more typical of calamitic compounds.

3.3.6.1 4,6-Dichloro-1,3-phenylene bis[4-(4-n-alkyloxy-3-fluoro-phenylimino-methyl)benzoates] (19)

Phase behavior

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</table>

* The calorimetric peaks of SmA-N and N-I transition could not been resolved. The sum of these transition enthalpies: $\Delta H$ (SmA-N) + $\Delta H$ (N-I) = 2.0 kJ/mol

~The transition is not observable on the DSC

Table 3.14 Transition temperature (°C) and enthalpy values [kJ/mol] of 19.1-19.5 provided by DSC measurements
These compounds exhibit “conventional” nematic and smectic as well as banana mesophases. The latent heat of SmC-SmCP transition is very small and strongly depends on the cooling rate. Such behavior implies the transition be of weakly first order. Furthermore SmCP mesophase appears only on cooling. The melting point slightly decreases, whilst the clearing point marginally increases with increasing chain length.

Texture observations and electro-optical investigations

Upon cooling of the isotropic liquid, SmA phase appears either as black homotropic texture or as fan-shaped texture.

Fig. 3.21 Weakly birefringent texture of the SmC phase at 130°C (compound 19.5)

Fig. 3.22 Frozen schlieren texture of the SmCP phase at 95°C in compound 19.5
In the SmC phase the fan-shaped texture becomes broken and characteristic pattern caused by long-wave director fluctuations is visible. When the phase is formed by homeotropic texture of the SmA phase, schlieren texture with very weak birefringence appears what indicates that the tilt angle in the SmC phase might be quite small (Fig. 3.21).

During the transition from the SmC into the SmCP phase the fluctuation of the \( c \) director (projection of the molecular long axis on the smectic layer) becomes less intensive resulting in a “frozen” schlieren pattern of SmCP phase. Meanwhile the contrast of the texture increases (Fig. 3.22). At the same time switching appears in respond to the external electric field. The extinction brushes of the fan-shaped texture experience small turns clock- and anticlockwise depending on the polarity of the external field. When the external field goes off the switched state relaxes in the initial state. These findings stand for antiferroelectric nature of the low-temperature mesophase and the anticlinic \( \text{SmC}_A \text{P}_A \) ground state. These compounds show a pronounced temperature dependence of the spontaneous polarization in the SmCP phase (Fig. 3.23).

![Fig. 3.23](image)

**Fig. 3.23** Temperature dependence of the spontaneous polarization in compound 19.5

*NMR measurements*

There is just a slight temperature dependence of the order parameter \( S=0.57-0.66 \) in the SmA and SmC phases, however, during the transition from the SmC into the SmCP phase the orientational order parameter is essentially constant. The bending angle
\(\alpha\) has been estimated on the base of \(^{19}\text{F}-\text{NMR}\) measurements. The temperature dependence of the bending angle is illustrated in Fig. 3.24. In the SmA phase the molecule is, actually, stretched: the bending angle is close to 160 deg. There is just a slight decrease of the angle \(\alpha\) in the SmC phase and the bending angle decreases considerably in the SmCP phase. This decrease is continuous and over a large temperature interval. In the meantime, the minimum value of the bending angle is just around 145 deg, considerably deviating from the temperature independent \(\alpha\) of 120 – 115 deg of the other fluorinated compounds 13.1, 21.1 and 21.2 with the I \(\rightarrow\) SmCP polymorphism.

**Fig. 3.24** Temperature dependence of the bending angle in compound 19.5

**X-ray measurements**

All three mesophases (except for the nematic) show quasi-Bragg reflections from a layer structure as well as a wide-angle diffuse scattering appearing from the liquid-like order within the smectic layers. The layer spacing exhibit very weak temperature dependence for all compounds. In the SmA phase the \(d\)-values are smaller than the molecular length (Table 3.15). The experimental data can be well fitted by linear func-
tion giving the following dependence of the layer spacing on the length of the terminal chain \( n \): \( d = 36.08 + 1.12n \) (Å). Normally, the layer spacing \( d \) is proportional to the two-fold value of terminal chain length \( n \). This implies that the molecules in the SmA phase are intercalated.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Sign} & \text{layer spacing} & \text{molecular length} & \text{length of the aliphatic chain} \\
& d \text{ (Å)} & L_{str} \text{ (Å)} & L_{al} \text{ (Å)} \\
\hline
19.1 & 44.8 & 52.0 & 11.2 \\
19.2 & 46.1 & 52.6 & 12.6 \\
19.3 & 47.9 & 58.0 & 14.1 \\
19.4 & 48.3 & 60.8 & 15.4 \\
19.5 & 49.3 & 62.8 & 16.8 \\
\hline
\end{array}
\]

Table 3.15 Layer spacing \( d \), molecular length \( L_{str} \) and the length of the aliphatic chains \( L_{al} \) in compounds 19.1-19.5 in SmA phase

In the SmC phase the layer spacing slightly decreases by 0.5–1 Å depending on the homologue. X-ray measurements performed on the oriented samples show that the patterns of all three mesophases SmA, SmC and SmCP look very similar. The \( \chi \)-scan in the SmC phase is just slightly broader than in the SmA phase, which means that the molecular tilt should not exceed 2–4 degrees. In the SmCP phase the broadening is larger, however, no splitting is observed and the corresponding tilt angle is smaller than 5–7 degrees in agreement with results of the electro-optical measurements.

**Dielectric measurements**

In both types of compounds, with SmA-SmCP and SmC-SmCP transitions one relaxation process was observed in the paraelectric phases (SmA, SmC) and two relaxation processes were found in the antiferroelectric SmCP phase. The relaxation process in the paraelectric phases can be attributed to the rotations about the long molecular axis. The dielectric strength of this process shows a critical-like behavior in vicinity of
the transition into the antiferroelectric phase. Such behavior can be explained with the help of Landau-Ginsburg theory of paraelectric-ferroelectric transitions.

In the antiferroelectric phase there are two relaxation processes from 100 to 1 kHz and from 10 to 0.1 Hz. The dispersion curve of the high-frequency process in the paraelectric phase seems to proceed as the high-frequency process of the antiferroelectric phase. However, the two curves have discontinuity at the transition point. Therefore the high frequency process in the antiferroelectric SmCP phase does not have to correspond to the rotation about the long molecular axis. The low-frequency process corresponds to the relaxation time equal to the switching time provided by electro-optical measurements. Hence, one possible explanation is that these processes are attributed to the ferro- and antiferroelectric modes of the polarization fluctuations [94, 98].

### 3.3.6.2 4,6-Dichloro-1,3-phenylene bis[4-(4-n-alkyloxy-2-fluoro-phenylimino-methyl)benzoates] (20)

![Chemical structure of 4,6-Dichloro-1,3-phenylene bis[4-(4-n-alkyloxy-2-fluoro-phenylimino-methyl)benzoates]](image)

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*Table 3.16* Transition temperature (°C) and enthalpy values [kJ/mol] of 20.1 and 20.2 provided by DSC measurements

These compounds exhibit a monotropic nematic and the long chain homologue an additional enantiotropic SmC mesophase. The mesophases are typical of rod-like
molecules again what means that the molecules are conceivably stretched. As expected, all transitions are observable on the DSC curves (Table 3.16).

The following comparison can be made between the non-fluorinated* [40] and the fluorinated substances 19.1-19.5 and 20.1, 20.2:

- all compounds exhibit high-temperature mesophases in which the molecules have stretched conformation (the bending angle is alike to rod-like molecules),
- the long-chain non-fluorinated compound exhibit a SmC, a SmC and a nematic phase (with increasing temperature) [40],
- in compounds 19.1-19.5 an additional monotropic switchable low-temperature SmCP mesophase emerges,
- in 20.1 the nematic phase becomes monotropic, and only the long-chain homologue 20.2 exhibits SmC mesophase,
- in conclusion the fluorination in position of X favorably influences the polymorphism of 4,6-dichlororesorcinol bananas.

* The 4,6-dichloro-1,3-phenylene bis[4-(4-n-alkyloxyphenyliminomethyl)benzoates], the non-fluorinated mesogens have the following phase behavior [40]: if n=8 Cr 126 N 148 I and if n=12 Cr 148 SmC 113 SmC 121 N 137 I.
3.3.7 5-Fluororesorcinol derivatives

In this section you will read about bent-core mesogens exhibiting unique polymorphism of B$_5$ mesophases [99]. Additionally, these compounds are the first mesogenic 5-substituted-resorcinol derivatives with non-perfluorinated terminal chain.

3.3.7.1 5-Fluoro-1,3-phenylene bis[4-(4-n-alkyloxy-3-fluoro-phenyliminomethyl)benzoates] (21)

From the homologue serie (n=8-12) the compound 21.1 and 21.5 were thoroughly investigated. Since identification of the mesophases requires long electro-optical and NMR studies, the mesophases exhibited by the compounds n=9-11 cannot be unambiguously provided. Furthermore, the difference between SmCP (B$_2$) and B$_5$ mesophases can be seen only on cooling in polarizing microscope, the XRD measurements on powder sample were also made on cooling. Thus, the transition temperature and enthalpy values obtained on cooling are given. The phase sequence except for the octyloxy and dodecyloxy homologues is a preliminary.

![Fig. 3.25](image_url) The phase behavior of substances 21.1-21.5. The phase assignment is a preliminary for the substances 21.2-21.4. The B$_{5A}$ subphases could not be distinguished by means of DSC.
### Table 3.17

Transition temperature (°C) and enthalpy values [kJ/mol] of compounds 21.1-21.5 on cooling. * means supposed phase.

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<th>B₅A‴</th>
<th>B₅A‴</th>
<th>B₅A‴</th>
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</table>
Polarizing microscopy and electro-optical investigations

On cooling the isotropic liquid the SmCP (B\textsubscript{2}) mesophase appears as a non-specific grainy texture. A kind of schlieren texture could be obtained by shearing the sample. At the transitions into the low-temperature phases the texture does not markedly change. Nevertheless for a fast heating or cooling rate these phase transitions have also been recognized by a minor change of the paramorphic textures. Fan-shaped domains have been obtained using a sufficiently high electric field. At the transition B\textsubscript{2} $\rightarrow$ B\textsubscript{5A} the fan-shaped texture becomes more flat. A considerable change has been observed at the transition into B\textsubscript{5F} when a constriction of the texture has been seen and the fans become broken, but there is no change in texture at the transition into the solid state.

Above the threshold the initial bright birefringent ribbon texture of the B\textsubscript{2} phase transforms into a smooth SmA-like fan-shaped texture. When the field is removed, the texture switches back into the initial state. The textures of the switched state are independent of the sign of the applied field what points to a racemic ground state. At the transition from the B\textsubscript{2} into the B\textsubscript{5A} phase the threshold slightly increases from 0.6 V/\(\mu\)m until 1.3 V/\(\mu\)m, however, the change of the textures on switching looks similar to the case of the B\textsubscript{2} phase (Fig. 3.26).

In the B\textsubscript{5F} phase the texture of the switched states does not relax or change anyway when the external field is removed. The switching into another polarized state takes place only when the field of opposite polarity (higher than the threshold field) is applied. In contrast to the B\textsubscript{2} and B\textsubscript{5A} phases, the textures of the switched states are different for opposite signs of the electric field, that means, dark domains became bright and vice versa.

There is a remarkable difference between the appearance of the antiferroelectric B\textsubscript{5A} phase on cooling and heating. On heating from the B\textsubscript{5F} phase, some homochiral domains remain, where the texture is different for an opposite sign of the applied field. In contrast, on cooling from B\textsubscript{2} the B\textsubscript{5A} phase appears as a racemic one. In the B\textsubscript{2} phase only a racemic ground state has been observed. The hysteresis curves of the B\textsubscript{5A} and B\textsubscript{5F} phases are illustrated in Fig. 3.27. The value of spontaneous polarization slightly changes between the mesophases.
Fig 3.26 Optical textures of the B_{sym} phase in compound 21.5 at 125°C a) $E=0 \text{ V} \mu\text{m}^{-1}$ b) $E=0.6 \text{ V} \mu\text{m}^{-1}$ c) $E=1.6 \text{ V} \mu\text{m}^{-1}$
Fig. 3.27 Hysteresis curves of the B_{5A} (red) and the B_{5F} (blue) mesophases

**X-ray investigations**

Although the compounds under investigation possess quite a large number of mesophases, only two kinds of X-ray patterns could be observed: one typical of the SmC or B\textsubscript{2} and the other one typical of the B\textsubscript{5} phases. The high temperature phase exhibits a pattern without in-plane order, typical for SmCP: the layer reflections are observed on the meridian of the pattern; the maxima of the broad outer diffuse scattering are situated out of the equator indicating an inclination of the molecules and the absence of the long-range positional order within the layers. There are two kinds of scattering centers in the low-temperature phases: ordered in a rectangular two-dimensional lattice (the molecules from different layers are not correlated) and disordered centers that give a broad diffuse halo. Such behavior is characteristic for B\textsubscript{5} phases. No discontinuous change has been seen at the phase transition temperatures observed in the DSC below the B\textsubscript{2} phase. The layer spacing $d$, obtained from the powder samples is nearly independent of the temperature for the short-chain homologue 21.1, whereas in the long-
A slight temperature dependence of the $d$-values has been observed.

**NMR studies**

In these compounds there are fluoro-substituents on the central as well as on the outer rings. Therefore order parameter and the bending angle $\alpha$ could be obtained from $^{19}\text{F}$-NMR measurements. The fluoro-substituent on the central ring provides a triplet representing the dipole interaction between the fluorine and the neighboring protons, the fluoro-substituents on the outer rings produce a doublet as a result of the dipole splitting of these fluorines. The splitting of the triplet can be written as

$$\Delta \nu_{\text{C}}^F = \Delta \nu_{\text{C}}^F S$$  

where $\Delta \nu_{\text{C}}^F = -15.08$ ppm is an interaction constant defined by the geometry of the central ring.

The splitting of the fluorines on the outer rings can be written as

$$\Delta \nu_{\text{A}}^F = \Delta \nu_{\text{A}}^F S\left(\frac{3}{2} \cos^2(\varepsilon) - \frac{1}{2}\right)$$

where the splitting constant $\Delta \nu_{\text{A}}^F = -28.0$ ppm.

This tendency of splitting could be observed in all phases. Therefore it was assumed that the angle $\varepsilon$ (the angle between the molecular and the para axis of the molecule) in low temperature phases has similar values to those in the high temperature phase. However, poor orientation in the B$_5$ phases resulted in broadening of the peaks. The bending angle $\alpha$ ($\alpha = 180 - 2\varepsilon$) was found to be around 116-118 deg. The order parameter $S$ is nearly temperature independent in the B$_2$ phase, and slightly decreases in the B$_{5A}$ phase reaching its maximum of 0.9 in the B$_{5F}$ phase (Fig. 3.28).
Chapter 3 Substituted resorcinol derivatives

3.3.7.2 5-Fluoro-1,3-phenylene bis[4-(4-n-alkyloxy-2-fluoro-phenyliminomethyl) benzoates] (22)

![Chemical structure of compound 22]

<table>
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<td>139</td>
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<td>22.2</td>
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<td>137</td>
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</table>

* summ of ΔH value of both transitions, the peaks could not be separated

| Transition temperature (°C) and enthalpy values [kJ/mol] of compounds 22.1 and 22.2 |

*Table 3.18*
3.3.7.3 5-Fluoro-1,3-phenylene bis[4-(4-n-alkyloxyphenyliminomethyl)benzoates]
(23)

5-fluororesorcinol derivative bananas had not been prepared before the beginning of this work. Therefore not only should the compounds 21 and 22 have been synthesized but also the substances without fluoro-substituents on the outer rings.

Phase behavior (DSC)

These compounds exhibit enantiotropic SmCP (B$_2$) mesophase. Chain lengthening decreases the melting and clearing points. Accordingly, the mesophase range becomes narrower with increasing chain length. Compound 23.1 was studied in detail and will be described below.

![Chemical structure](image)

<table>
<thead>
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<td>[12.3]</td>
<td>[23.8]</td>
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<tr>
<td>23.2</td>
<td>12</td>
<td>•</td>
<td>149</td>
<td>169</td>
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<td>[15.6]</td>
<td>[27.9]</td>
</tr>
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Table 3.19 Transition temperature (°C) and enthalpy values [kJ/mol] of compounds 23.1 and 23.2

Texture observations and electro-optic measurements

The SmCP phase appears from the isotropic phase as a fine grainy texture (Fig. 3.24). When the cooling rate is slow (0.1 K/min) a fan-shaped texture can be observed.
Application of an electric field leads to electro-optical switching. This process has a threshold of about \(~1.5\) V/\(\mu\)m. The switched state is independent of the polarity of the external field. The switching polarization does not show any temperature dependence. The polarization values are quite high (\(~640\) nCcm\(^{-2}\)).

![Grainy texture of SmCP phase in compound 23.2](image)

**Fig. 3.29** The grainy texture of SmCP phase in compound 23.2

*X-ray investigation*

X-ray measurements on non-oriented samples showed the layer reflections up to the second order and broad diffuse scattering in the wide-angle region. The \(d\)-values are temperature independent (\(d=37.5\) Å). Experiments on oriented samples provided some more information about the structure of the mesophases. The splitting of the outer diffuse maxima indicates a tilted arrangement of the molecules in the smectic layers, which is compatible with the SmCP phase. The splitting does not show any temperature dependence.

*NMR studies*

The symmetry of the molecule defines the molecular axis perpendicular to the C-F bond in the central ring. The \(^{13}\)C-NMR spectra of the central ring provide us with eight parameters: four shift anisotropies and four C-F dipolar couplings. These data are enough to estimate both a transversal order parameter \(S\) and the longitudinal order pa-
rameter $D$. However, poor resolution of the central ring carbons complicates experimental realization.

The splitting observed in $^{19}$F-NMR spectra is governed by the dipolar interactions between the fluorine and the neighboring protons. The spectrum consists of a triplet of (overlapped) doublets. This additional splitting between the two peaks of a doublet gives another way to estimate the transversal order parameter. The longitudinal order parameter was found to be $S = 0.875$, the transversal order parameter $D = 0.006$.

Comparing the fluorinated (21 and 22) and non-fluorinated (23) substances described above the following can be outlined:

- substances 23.1 and 23.2 exhibit SmCP mesophase,
- fluorination on the outer rings in position 2 drastically reduces (22.2), even vanishes (22.1) the phase existence,
- fluorination on the outer rings in position 3 (21.1-21.5) has a completely different influence: not only do SmCP phase exist, but low-temperature B$_5$ mesophases appear, too.

Furthermore 5-chloro-1,3-phenylene bis[4-(4-octyloxyphenyliminomethyl)benzoate] (24) was prepared. This compound is not liquid crystalline: it melts at 150°C and freezes at 136°C.