

THERMOTROPIC LIQUID CRYSTALS

Thermotropic Liquid Crystals

Recent Advances

Edited by

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PREFACE

Liquid crystalline materials are omnipresent in daily life. A broad spectrum of powerful applications of these exotic materials has created new avenues in academic and industrial research. Some of the common applications include display devices, temperature and pressure sensors, light valves and biosensors. Yet, there is considerable current interest in the design and development of novel liquid crystalline compounds with various functional properties. In addition, there is a significant interest in the characterization of these compounds at atomistic-level resolution using a variety of modern experimental, theoretical and computational approaches, which would aid the easy creation of high quality functional molecules. The mesogenic properties of liquid crystalline molecules are fascinating to spectroscopists and have been well utilized in the development of a variety of physical techniques including Nuclear Magnetic Resonance spectroscopy. Needless to mention that the increasing number of research teams, reports and meetings related to this interdisciplinary field is an indication of the wealth and remaining challenges of this rapidly growing field.

This book does not intend to cover the whole field of thermotropic liquid crystalline (TLC) materials as it is extremely difficult to cover within a single book. Instead it presents a collection of Chapters written by experts on various exciting topics in the field. Properties of recently developed TLCs (such as banana-type, thiophene-based, and columnar TLCs), phase biaxiality, and novel polymeric TLCs are discussed in detail. Solid-state NMR studies to obtain atomistic-level structural and geometrical information of TLCs are presented. Synthesis of liquid crystalline conjugated polymers, fast switching of nematic materials by an electric field, and photoconducting discotic systems are also presented.

It is my considerable pleasure to offer my thanks to all the authors for their wonderful contributions and the publishers for the help in developing the book. I thank my family for their help in bringing out this book. I also would like to thank my colleague and friend, Dr. Narasimhaswamy (Central Leather Research Institute, Chennai, India), who introduced me to this exciting field of research that has led to the development of this book.

I sincerely hope researchers in both academia and industries will find the book to be useful for their research.

Ann Arbor,
Michigan, USA
October 17, 2006

Ayyalusamy Ramamoorthy
The University of Michigan

CHAPTER 1

MESOPHASE BEHAVIOUR AT THE BORDERLINE BETWEEN CALAMITIC AND “BANANA-SHAPED” MESOGENS

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1. INTRODUCTION

Organic compounds with pronounced shape anisotropy (rod-like or disc-like) are able to form thermotropic mesophases. Rod-like (calamitic) mesogens can exhibit nematic as well as different smectic phases characterized by a layered structure. Disc-shape mesogens preferably form columnar phases of different type characterized by a 2D superstructure. In rare cases they can also form nematic phases. Nematic phases may be characterized as the simplest liquid crystalline phase which is distinguished from the isotropic liquid only by the long-range orientational order. It is possible to describe the spontaneous parallel orientation of the molecules in nematic mesophases only by the anisotropy of repulsive forces coupled with the isotropic part of the dispersion interaction [1, 2]. It does not exclude that in dependence on the molecular structure – especially for the formation of smectic layer structures or columnar structures – other intermolecular interactions can play an important role (e.g. polar forces, charge-transfer complexes, hydrogen bonds). But in addition, the interaction between chemically incompatible moieties [3] as well as special steric interactions can clearly influence the structural features of mesophases. Special steric interactions may occur, if the molecular shape strongly deviates from the classical rod-like (or disc-like) shape. Elongated molecules with bulky branches at the ends of the molecules, the so-called polycatenar compounds are well-known examples. These compounds are able to form not only nematic or smectic phases but also mesophases with 2D superstructure (columnar phases) or 3D superstructure (cubic, tetragonal, rhombohedral phases) [4, 5]. Another impressive example of

a special steric interaction is molecules with a pronounced bent shape which are the topic of this chapter. Such substances were already synthesized by Vorländer et al. 1932 [6] and later by Akutagawa et al. [7], but it were Niori et al. [8] who discovered the polar properties of smectic phases formed by bent molecules. It was shown that due their bent shape the molecules can preferably be packed in bent direction giving rise to a long-range correlation of the lateral dipole moments, that means to a macroscopic polarization in the smectic layers.

In the following the most important mesophases formed by bent molecules shall be briefly characterized. In the SmAP phase (P means polar) the molecules are arranged perpendicular to the layers like in SmA phases but they possess a polar packing (in bent direction) within the layer plane. Depending on the direction of the polar axes in adjacent layers the SmAP phase can behave ferroelectric (polar axes parallel) or antiferroelectric (polar axes antiparallel) which is indicated by the subscripts F or A (SmAP_F , SmAP_A).

In most cases the polar packed bent molecules are tilted with respect to the layer normal. In analogy to the SmAP phase this phase is designated as SmCP which can either be ferroelectric (SmCP_F) or antiferroelectric (SmCP_A). But in addition, in the case of SmCP phases we have also to distinguish – with respect to the tilt direction – between synclinic or anticlinic interlayer correlation which is indicated in the phase symbol by the subscripts S or A after C. That means, four structural types of the SmCP phase are possible – SmC_SP_A , SmC_AP_A , SmC_SP_F , SmC_AP_F – which are schematically presented in Figure 1-1 [9]. Another aspect is of fundamental interest. The combination of director tilt and polar order leads to the chirality of smectic layers although the constituent molecules are achiral [9, 10]. As shown in Figure 1-1 two equivalent layer structures with antiparallel polar axes exist for a given tilt direction but these structures are mirror images from each other. In Figure 1-1 the opposite chirality is depicted by red or blue molecule symbols. In the so-called “racemic” states (SmC_SP_A , SmC_AP_F) the chirality alternates from layer to layer. In the “homochiral” states (SmC_AP_A , SmC_SP_F) the layer chirality

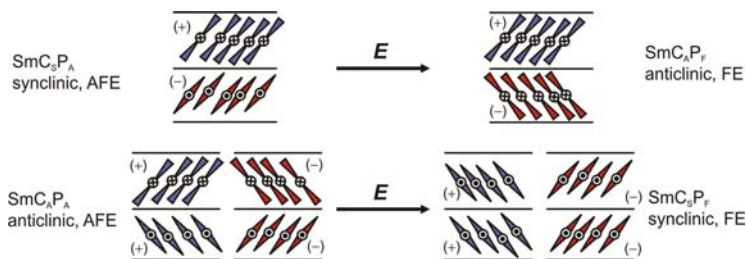


Figure 1-1. The molecular arrangement considering tilt and polarity in adjacent layers of bent-core molecules. The smectic layers are perpendicular to the drawing plane. The different molecule symbols (\times), (\bullet) correspond to opposite bent direction perpendicular to the drawing plane, i.e. to opposite polar axes. Red and blue molecule symbols indicate layers of different chirality. The arrows indicate the field-induced transition of the antiferroelectric into the ferroelectric state (AFE = antiferroelectric; FE = ferroelectric)

is uniform within a macroscopic domain. In order to escape from the macroscopic polarization, SmAP as well as SmCP phases have mostly an antiferroelectric ground state (alternating polarization in adjacent layers) which can be switched into corresponding ferroelectric states (indicated by arrows in Figure 1-1). This switching (also the switching between the opposite ferroelectric states) usually takes place by the collective rotation of the molecules around the tilt cone like in SmC* phase of calamitic compounds. It can be seen from Figure 1-1 that during the switching the chirality of the layers (red and blue, resp.) does not change.

Another way to avoid bulk polarization in layered structures of bent molecules is to break the layers into 2D modulated structures which can be regarded as columnar structures where the layer fragments represent the columns. In many cases the columnar phases of bent molecules have a rectangular cell (formerly this Col_r phase was also designed as B₁), but there are also examples of an oblique lattice (Col_{ob}) [11–16]. It seems that the columns consisting of layer fragments are polar ones but the macroscopic polarization is avoided by an antiparallel alignment of the polar axes.

It should be mentioned that further phases are formed by bent-core mesogens, which, however, have no relation to the subject of this chapter. Concerning the structure of the B₃, B₄, B₅, B₆ and B₇ phases, we refer therefore to three reviews on banana-shaped liquid crystals [12, 16, 17]

The assignment of the mesophases is based on different experimental techniques. Phase transitions are usually detected by calorimetry but also by polarizing optical microscopy. Textural features obtained by polarizing microscopy give first hints about the mesophase type. The most important method for the structural characterization is X-ray diffraction measurements. If possible these measurements should be performed on oriented samples. The polar properties are investigated by current response measurements, mostly using the triangular wave voltage method [18]. Information about the molecular dynamics can be obtained by dielectric measurements [19–21]. NMR spectroscopy allows the determination of the orientational order parameter by ¹H splitting or ¹³C anisotropic shift measurements. Using the experimental order parameter the conformation of the bent molecules in the liquid crystalline state may be estimated by ¹³C NMR [22–25], ¹⁹F NMR [26] or ²H NMR [26–28]. The knowledge of the conformation (especially of the bending angle) is important to understand basic relationships between molecular structure and the mesophase behaviour.

Since the discovery of the polar properties in smectic phases of bent-core mesogens in 1996 [8] chemists have synthesized a large variety of banana-shaped compounds with quite different structure. In most cases the chemical structure corresponds to the molecular design sketched in Figure 1-2.

The molecules consist of at least five rings connected by the linking groups X, Y. The two legs are attached to the central part, which introduces the bending angle in the whole molecule. Mostly the bending angle of about 120° results from the 1,3-phenylene disubstitution, as shown in Figure 1-2. The central phenyl ring can be replaced by naphthalene or by six- or five-membered heterocyclic

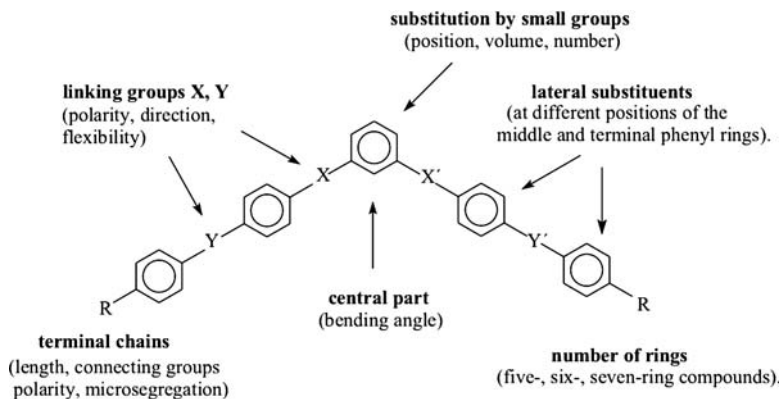


Figure 1-2. Molecular design of bent-core mesogens

rings (e.g. pyridine, oxazole, oxadiazole). But also a short odd-numbered spacer consisting of one (-O-; -S-; -CH₂-; -CO-) or three single units (e.g. -CH₂OOC-) can be used to introduce the bending angle. The terminal rings are substituted by long hydrocarbon chains in most cases. Aliphatic chains containing perfluorinated moieties or siloxane containing fragments increase the effect of microsegregation in the resulting mesophases. Polar as well as non-polar groups can be attached at the different lateral positions of the phenyl rings which is a successful way to create new phases and phase sequences in banana-shaped liquid crystals. It will be shown that the influence of lateral substituents is of great importance with respect to the subject of this chapter. More detailed information about the relationship between the chemical structure of bent-core mesogens and their mesophase behaviour has been summarized in some reviews [12, 16, 17, 29, 30].

In principle the molecular design to prepare banana-shaped liquid crystals sketched in Figure 1-2 works, but until now some essential questions could not be answered in a satisfying way. An important question is, for example: What are the structural preconditions of bent-core molecules to form definite phases with polar structure or polar structural fragments (“banana phases”). There are bent molecules which form only the classical mesophases of calamitic mesogens, that means nematic or smectic phases. On the other hand, there are bent-core compounds which are able to form nematic and/or smectic phases as well as “banana phases”. This indicates that there is a more continuous borderline between bent-core and calamitic mesogens.

In order to get more insight into this borderline we present at first representative examples where “banana phases” as well as nematic and/or conventional smectic phases are observed at the same compound in quite different polymorphism variants. In cases where information about the detailed conformation of the molecules in the mesophases and its change with temperature are available, we will discuss the molecular origin of such complex phase behaviour. Furthermore, in a brief

section we will show that also in binary systems between bent-core and suitable calamitic mixing components and in dimers consisting of a calamitic and a bent-core mesogenic unit phase sequences with “banana phases” and nematic and smectic phases can be realized. An important part is devoted to structural features of nematic or smectic phases of bent compounds which can be manifested in unusual properties, for example unusual electro-optical behaviour.

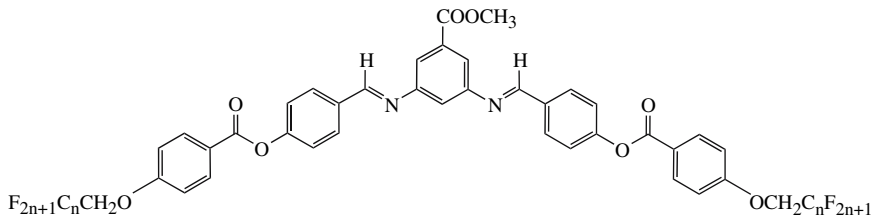
2. VARIANTS OF POLYMORPHISM WITH SmCP_A, CONVENTIONAL SMECTIC (SmA, SmC) AND NEMATIC PHASES

2.1 Dimorphism SmA-SmCP_A in Bent-core Mesogens with Perfluorinated Terminal Chains

The first examples of bent-core mesogens which form a polar SmCP_A phase as well as a SmA phase were reported in 2000 [31]. These five-ring compounds possess a CH₃OOC-substituent in 5-position of the central core and perfluorinated terminal chains (Table 1-1).

The high-temperature smectic phase exhibits a homeotropic or a fan-shaped texture which is typical for a SmA phase. In contrast, the low-temperature phase forms a schlieren or a grainy texture, respectively, and shows a polar electro-optical response since the texture of the switched state depends on the polarity of the applied field. Current response measurements give evidence for an antiferroelectric ground state which can be switched into corresponding ferroelectric states. On the base of these experimental findings the low-temperature phase could be identified

Table 1-1. Transition temperatures (°C) and enthalpy changes (kJ mol⁻¹; in square brackets below the temperatures) of the compounds **1a-1b**



No	n	Cr	SmCP _A	SmA	I			
1a	9	•	160 [20.6]	•	165 [6.7]	•	250 [1.8]	•
1b	11	•	175 [19.0]	•	182 [8.8]	•	265 [1.9]	•

Cr: crystalline; SmCP_A: antiferroelectric polar smectic C phase; SmA: smectic A phase; I: isotropic liquid; The numbers between the phase symbols designate the phase transition temperatures in °C, the numbers below which are the transition enthalpies in kJ mol⁻¹ (in square brackets).

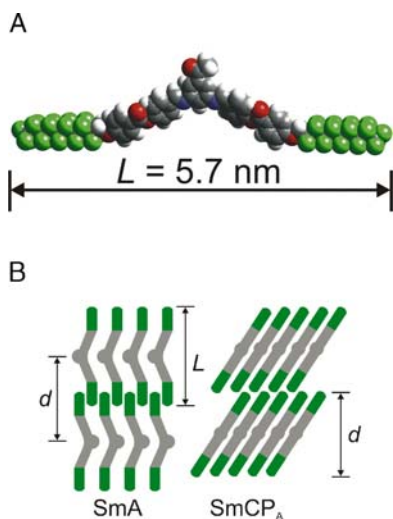


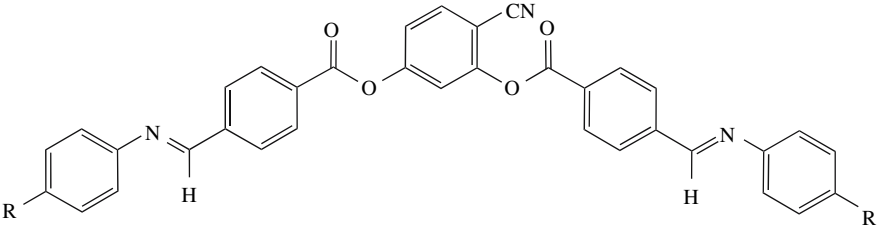
Figure 1-3. a) Molecular model of compound **1a**; b) Structure model of the SmA and SmCP_A phase of compounds **1** (copyright (2000) from Liq. Cryst. by L. Kovalenko et al., ref. 31. Reprinted by permission of Tayler & Francis, LLC.<http://www.taylerandfrancis.com/>)

as an antiferroelectric SmCP phase. It was found that the layer spacing d (47 \AA for compound **1a**) is clearly smaller than the molecular length L (57 \AA for compound **1a**), but surprisingly d is nearly the same in the SmA and the tilted SmCP_A phase. It is known from NMR measurements and X-ray studies on the SmA phase of analogous three-ring compounds that the difference between L and d is in the order of magnitude of the length of a terminal chain (similar to compounds **1a** or **1b**). Therefore it can be assumed that in the SmA phase the perfluorinated chains are more or less interdigitated (Figure 1-3). At the transition into the SmCP_A phase the interdigitation disappears and the molecules are tilted now. That means, both smectic phases possess a different packing of the molecules in the layers. This clear structural change is also indicated by the relatively high transition enthalpies (see Table 1-1).

2.2 Polymorphism SmA-SmCP_A, SmA-SmC-SmCP_A and N-SmA-SmC-SmCP_A in Cyano-substituted Bent-core Compounds

Five-ring bent-core compounds derived from 4-cyanoresorcinol represent the second substance class where phase sequences with SmCP_A phases and non-polar phases (N, SmA, SmC) have been observed [32].

It is seen from Table 1-2 that the dodecyl compound **2a** exhibits a dimorphism SmA-SmCP_A like compounds **1a** and **1b**. The other compounds show trimorphism

Table 1-2. Transition temperatures ($^{\circ}\text{C}$) and enthalpy changes [kJmol^{-1}] of the compounds **2a-2f**


No	R	Cr	SmCP _A	SmC	SmA	N	I
2a	C ₁₂ H ₂₅	• 80 [13.2]	• 124 [1.3]		• 164 [6.8]	–	•
2b	C ₁₄ H ₂₉	• 90 [19.5]	• 128 [1.8]	• 142 [–]	• 166 [7.6]	–	•
2c	C ₆ H ₁₃ O	• 122 [32.3]	• 103 [0.2]	• 133 [1.8]	• 156 [0.6]	• 165 [0.9]	•
2d	C ₈ H ₁₇ O	• 97 [37.4]	• 142 [1.9]	• 146 [2.1]	• 175 [4.8]	–	•
2e	C ₉ H ₁₉ O	• 62 [45.9]	• 134 [3.5]	• 138.5 [2.7]	• 180 [5.8]	–	•
2f	C ₁₂ H ₂₅ O	• 65 [14.7]	• 122 [4.8]	• 141 [–]	• 188 [7.2]	–	•

Cr: crystalline phase; I: isotropic phase; SmA, SmC: smectic A or smectic C phase, respectively; N: nematic phase; Parentheses indicate monotropic transitions.

SmA-SmC-SmCP_A or tetramorphism N-SmA-SmC-SmCP_A (compound **2c**). For the homologues **2c-2e** the phase transition SmA-SmC is of first order, the corresponding transition enthalpies vary between 1.8 and 2.7 kJmol^{-1} . The different smectic phases could be identified by polarizing microscopy, by electro-optical measurements and by X-ray investigations on oriented samples. The tilt angle of the SmC and SmCP_A phase is found to be relatively low and does not exceed 15° . Figure 1-4 shows the temperature dependence of the orientational order parameter *S* for the nematic, SmA, SmC, and SmCP_A phases of compounds **2c** determined by ^{13}C -NMR [32]. The bending angle – the opening angle between the two wings of the molecules – has been determined in the liquid-crystalline phases of compounds **2b** and **2c** by NMR studies. In the non-polar SmA and SmC phases the molecules possess a bent shape with a bending angle of about 140° which decreases to 135° in the SmCP_A phase [32]. It can be assumed that in the SmA phase the bent molecules can freely rotate around their long-axes giving rise to the uniaxial structure. In the SmC phase the molecules are weakly tilted ($\approx 15^{\circ}$) but according to dielectric measurements [33] ferroelectric clusters in the short-range order region exist. At a definite temperature the bending angle obviously reaches a critical value where the rotational barrier becomes strong and the polar packing with a long-range correlation of the lateral dipoles is favoured.

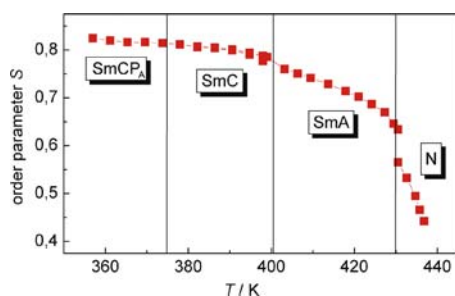


Figure 1-4. Temperature dependence of the orientational order parameter S in the nematic, SmA, SmC, and SmCP_A phase of compound **2c**

Table 1-3. Transition temperatures (°C) of the compounds **3a–3d**

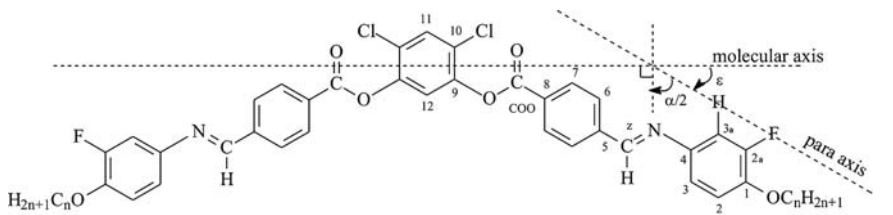
No.	n	A	B	Cr	SmCP _A	SmC	SmA	I				
3a [34]	12	F	H	•	75	•	129	•	133	•	182	•
3b [35]	12	Cl	H	•	87	•	112	–		•	168	•
3c [35]	8	CH ₃	H	•	110	(•	76	•	97)	•	117	•
3d [34]	8	H	CH ₃	•	90	(•	79)	–		•	107	•

In contrast to the compounds of series **1** the structural differences between the polar and non-polar smectic phases are less pronounced which is also indicated by the relatively low transition enthalpy SmA–SmCP_A or SmA–mCP_A. The main reason for the transition from the polar into the non-polar phases seems to be the clear decrease of the bending angle with decreasing temperature.

Starting from the parent series **2**, the attachment of lateral substituents (F, Cl, CH₃) at the outer rings can result in similar phase sequences, see for example compounds **3a–3d** in Table 1-3.

2.3 Five-ring 4,6-Dichlororesorcinol Derivatives with Fluorine or Chlorine Substituents at the Outer Rings

Also the following homologous bent five-ring compounds derived from 4,6-dichlororesorcinol show a similar mesophase behaviour which is summarized in Table 1-4 [22, 36].

Table 1-4. Transition temperatures ($^{\circ}\text{C}$) and enthalpy changes [kJ mol^{-1}] of the compounds **4a-4f**


No.	n	Cr	SmCP _A	SmC	SmA	N	I
4a	3	•	179 [75.9]	–	–	• (160)	• [1.3]
4b	8	•	127 [49.0]	• (95) [–]	–	• 130 [–] ^a	• 130.5 [–] ^a
4c	9	•	113 [44.4]	• (100) [0.5]	–	• 133 [4.2]	–
4d	10	•	108 [50.5]	• (103) [0.5]	–	• 137 [5.1]	–
4e	11	•	107 [52.8]	• (102) [0.3]	• 116 [–] ^b	• 139 [5.7]	–
4f	12	•	103 [57.1]	• (100) [0.2]	• 125 [–] ^b	• 139 [6.1]	–

^a) The calorimetric peaks of SmA-N and N-iso transition could not be resolved. The sum of these transition enthalpies: $\Delta H(\text{SmA-N}) + \Delta H(\text{N-iso}) = 2.0 \text{ kJ mol}^{-1}$.

^b) The transition is not observable by DSC.

Three distinct variants of polymorphism occur in dependence on the length of the terminal chains: N–SmA–SmCP_A for compound **4b**, SmA–SmCP_A for compounds **4c** and **4d** and SmA–SmC–SmCP_A for compounds **4e-4f** whereas the homologue with the shortest terminal chains **4a** forms a monotropic nematic phase, only. It follows from X-ray patterns of oriented samples and from electro-optical measurements that the tilt of the molecules in the SmC and SmCP_A phase is not larger than 8° . Similar to the homologues of series **2** the layer spacing d is nearly the same in all smectic phases and clearly smaller than the molecular length L . Considering the very low tilt angle the results of X-ray measurements can be interpreted by a partial interdigitation of the terminal chains not only in the SmA phase but also in the tilted smectic phases SmC and SmCP. Electro-optical investigations give evidence for an antiferroelectric ground state of the SmCP phase; the switching polarization shows a strong temperature dependence which is unusual for SmCP_A phases (Figure 1-5). On the other hand, the dielectric strength strongly increases on approaching the phase transition SmC \rightarrow SmCP_A (Figure 1-6a) or SmA \rightarrow SmCP_A (Figure 1-6b) which is characteristic for a transition from a paraelectric state (SmA, SmC) to a polar (ferro- or antiferroelectric) state. As shown in Figure 1-7 also in these compounds the bending angle ($\alpha = 180 - 2\varepsilon$; see formula in Table 1-4) decreases with decreasing temperature, e.g. it is 162° in the SmA phase and 155° to

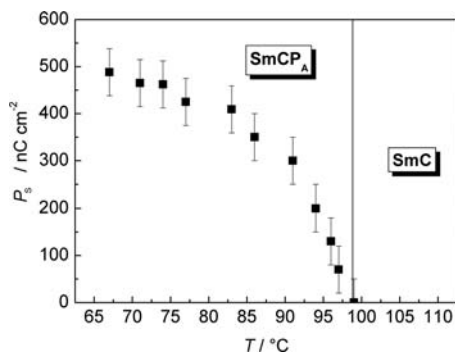


Figure 1-5. Temperature dependence of the switching polarization P_s in the SmCP_A phase of compound **4f** (reprinted with permission from ref. 22, copyright, 2004, The PCCP Owner Societies)

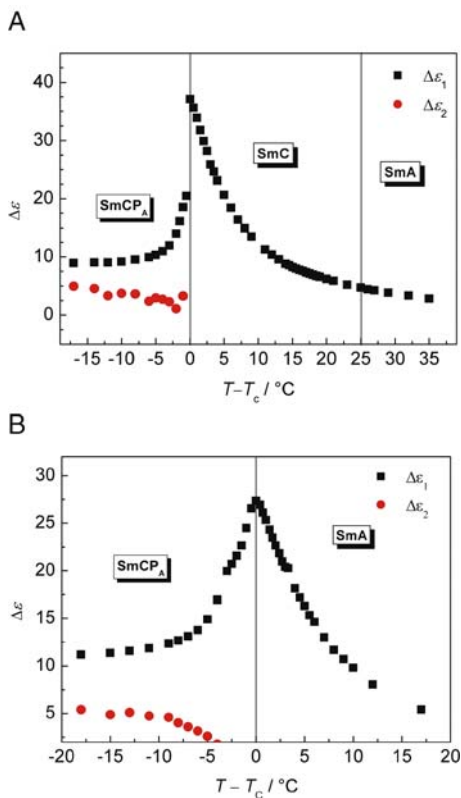


Figure 1-6. a) Dielectric strength in the SmA , SmC , and SmCP_A phase of compound **4f** plotted versus $T - T_c$ ($T_c = \text{SmC} - \text{SmCP}_A$ transition temperature); b) Dielectric strength in the SmA and SmCP_A phase of compound **4d** plotted against $T - T_c$ ($T_c = \text{SmA} - \text{SmCP}_A$ transition temperature) (reprinted with permission from ref. 22, copyright, 2004, The PCCP Owner Societies)

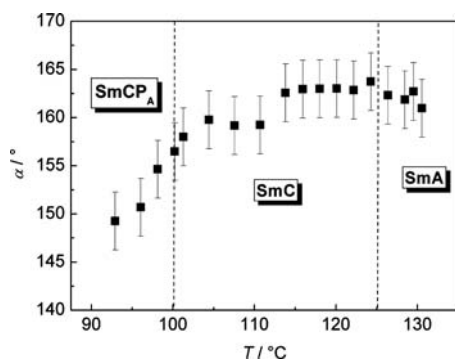


Figure 1-7. Temperature dependence of the bending angle α in the smectic phases of compound **4f** (reprinted with permission from ref. 22, copyright, 2004, The PCCP Owner Societies)

149° in the SmCP_A phase. That means, similar to the 4-cyanosubstituted compounds of series **2** and **3** the direct transition from a non-polar (SmA, SmC) into a polar smectic phase (SmCP_A) is related to the continuous decrease of the bending angle.

The only structural difference between series **4** and the next series **5** are the lateral substituents at the outer rings: here fluorine atoms are replaced by chlorine atoms, see Table 1-5 [37].

Table 1-5. Transition temperatures (°C) and enthalpy changes [kJ mol⁻¹] of the compounds **5a–5g**

No	n	Cr	SmCP _A	SmC	SmA	N	I
5a	5	• 128 [29.7]	–	–	–	(• 114)	• [0.8]
5b	6	• 114 [39.6]	–	–	–	(• 113)	• [0.7]
5c	7	• 115 [25.9]	–	(• 68)	–	• 111)	• [0.9]
5d	8	• 117 [65.9]	(• 71)	• 91	• 104	• 109)	• [1.3]
5e	9	• 101 [35.0]	• 75	• 105	• 112	–	• [3.2]
5f	10	• 103 [35.1]	(• 74)	• 112	• 118	–	• [4.7]
5g	12	• 106 [35.8]	(• 73)	• 121	• 122	–	• [5.1]

^aThis transition is not indicated by a calorimetric signal.

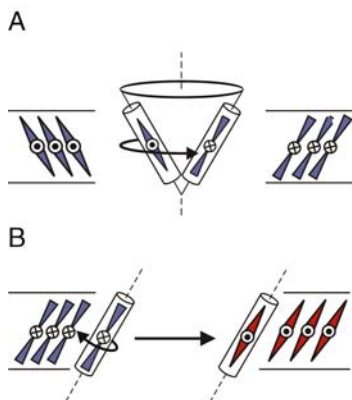


Figure 1-8. The possible mechanism of polar switching in the SmCP phases; a) Switching by collective rotation of the molecules around the tilt cone; b) Switching by collective rotation of the molecules around their long axes. Mechanism b) is accompanied by an inversion of layer chirality

Depending on the length of the terminal chains the homologues form a nematic phase, nonpolar smectic phases (SmA, SmC) and the polar smectic phase SmCP_A. It follows from X-ray measurements that the layer spacing d of the SmA phase is clearly smaller than the molecular length and it decreases only slightly on cooling into the tilted smectic phases which have a tilt angle not higher than 15°. Since the difference $L - d$ is in the order of magnitude of the length of the corresponding terminal aliphatic chain an intercalated structure of the smectic phases – as also found for the members of series **2** and **4** can be assumed. A significant difference to series **4** is the switching behaviour. The switching mechanism of the SmCP_A phase clearly depends on the temperature. At lower temperatures the switching takes place in the usual way by rotation of the director around the tilt cone. At higher temperatures the switching is based on the collective rotation of the molecules around the long axes which corresponds to the field-induced inversion of the layer chirality (Figure 1-8). Until now, such switching mechanism has been reported for SmCP_A phases of a few bent-core compounds, only [13, 38–41].

2.4 Polymorphism of the Non-polar SmC and/or the Nematic Phase with Several SmCP Phases

The homologues of the next series have a quite similar structure compared with series **2**, only the outer linking groups are ester groups instead azomethine groups [42]:

The common feature is that also in this series non-polar phases (N, SmC) as well as polar phases (SmCP_A) can occur at the same substance (Table 1-6).

Table 1-6. Transition temperatures ($^{\circ}\text{C}$) and enthalpy changes [kJ mol^{-1}] of the compounds **6a-6g**

No	n	Cr	Col	SmCP'' _A	SmCP' _A	SmCP _A	SmC	N	I
6a	6	• 105 [44.6]	–	–	–	–	–	• 140 [0.8]	•
6b	7	• 96 [37.7]	(• 68) [4.8]	–	–	–	–	• 132 [0.7]	•
6c	8	• 99 [52.0]	–	–	–	–	–	• 132 [0.8]	•
6d	9	• 92 [47.7]	–	–	–	–	–	• 128 [0.7]	•
6e	10	• 99 [66.1]	–	–	(• 66 [2.2]	• 77 [2.0]	–	• 128 [1.1]	•
6f	12	• 103 [65.7]	–	(• 68 [0.4]	• 75 [0.5]	• 94 [0.2]	• 109 [0.5]	• 129 [1.3]	•
6g	16	• 103 [65.7]	–	(• 74 [0.4]	• 79 [0.4]	• 99 [–] ^a	• 133.5 [6.3]	–	•

^a This transition could not be detected by calorimetry.

But there are some significant differences. With exception of the hexadecyloxy compound all homologues listed in Table 1-6 exhibit a nematic phase but a SmA phase does not occur. The decyloxy homologue **6e** forms two antiferroelectric SmCP_A phases whereas for the longer chained homologues the non-polar SmC and three SmCP_A phases could be distinguished by calorimetry although the transition enthalpies are very low. On the other side, also the textural changes are very small and X-ray investigations showed no significant differences between the SmCP_A phases. The phase sequences of the homologues **6e**, **6f** and **6g** were only observed in this series. Similar to the series **2** the terminal chains of the smectic phases are partially intercalated, but in contrast to series **2** the tilt angle of the smectic phases is clearly enhanced (between 30...35°). Another remarkable difference is the switching mechanism of the SmCP_A phases. The field-induced transition from the antiferroelectric ground state into the switched ferroelectric states preferably takes place through a collective rotation of the molecules around their long axes. Such switching mechanism is accompanied by an inversion of the layer chirality by reversal of the field polarity (see series **5**). It should be noted that also the nematic phase shows some unexpected properties which are obviously related to the bent shape of the molecules and which will be discussed in section 6.1.

2.5 Liquid Crystal Tetramorphism with a SmA Phase and a Reentrant SmC_SP_A Phase

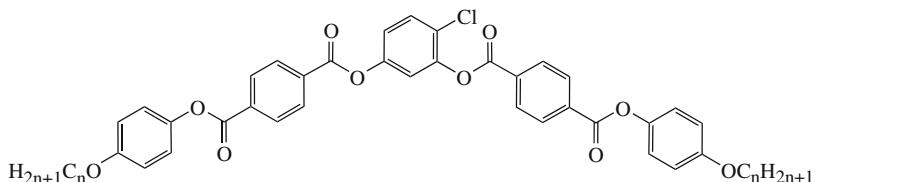
In long-chained members of a new series of five-ring bent-core compounds which contain a chlorine substituent in 4-position of the central phenyl ring and only ester linking groups between the rings, an unusual polymorphism variant occurs: SmA–SmC_SP_A–Col_{ob}–SmC_SP_A, see Table 1-7 [43].

This phase sequence is elucidated by X-ray diffraction measurements and detailed electro-optical investigations. The SmC_SP_A phases are structurally identical and differ only in the mechanism of polar switching. The switching of the high-temperature SmC_SP_A phase is based on the collective rotation of the molecules around their long axes whereas the switching of the reentrant SmC_SP_A phase takes place though the rotation of molecular long axes around the tilt cone. The Col_{ob}P_A phase can be transformed to the SmC_SP_F phase by the application of an electric field. The non-polar SmA phase shows a reversible field-induced transition into the SmC_SP_F phase in a limited temperature range which will be discussed in section 7.2.

It is remarkable to notice that the short chain homologues **7a** and **7b** exhibit only a SmCP_A phase, that means, lengthening the terminal chains (compounds **7c-e**) can induce a conventional smectic A phase in this series. That is in contrast to the relationships reported on banana-shaped liquid crystals up to now.

It should be noted that also in analogous compounds, however with 4,6-dichloro substitution, phase sequences with “banana phases” and nematic and conventional smectic phases occur, e.g. SmCP_A–SmA–N(n = 8); SmCP_A–SmC–SmA (n = 12) and SmCP_A–SmC (n = 16) [44].

Table 1-7. Transition temperatures (°C) and enthalpy changes [kJ mol⁻¹] of the compounds **7a-7e**

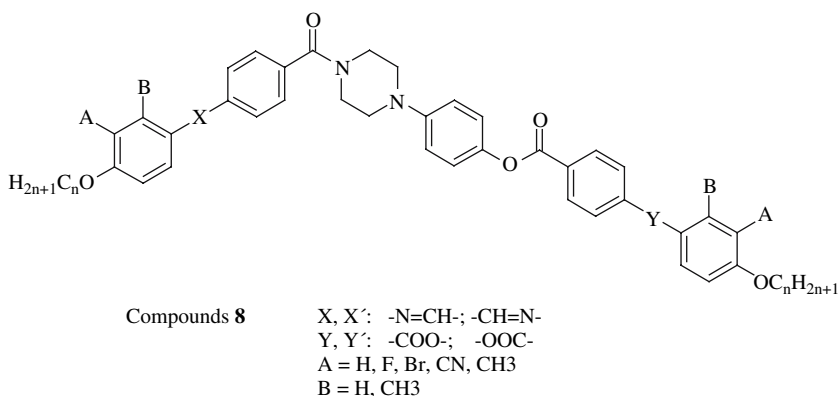


No	n	Cr	SmC _S P _A	Col _{ob} P _A	SmC _S P _A	SmA	I					
7a	8	•	113.0 [20.7]	•	145.0 [16.0]	–	•					
7b	12	•	110.0 [50.0]	•	147.0 [18.2]	–	•					
7c	14	•	105.0 [60.3]	•	134.0 ^a [–]	•	138.0 [0.8]	•	139.5 [2.2]	•	144.0 [8.8]	•
7d	16	•	108.0 [74.9]	•	130.0 ^a [–]	•	135.0 [1.5]	•	138.5 [2.7]	•	145.5 [8.6]	•
7e	18	•	107.0 [71.9]	•	123.0 ^a [–]	•	128.0 [1.4]	•	134.0 [3.1]	•	142.5 [8.7]	•

^a The enthalpy for this transition could not be determined.

2.6 Benzoyl Derivatives of Secondary Cyclic Amines

There are non-linear compounds where the bend of the molecule is not achieved by 1,3-substitution of the central aromatic ring. Weissflog et al. presented a new class of bent compounds in which the central fragment consists of a benzoyl derivative of a secondary cyclic amine. In this case a carbonyl group links the phenyl ring of one leg with the nitrogen of the piperidine or piperazine ring which is part of the second leg [45, 46]. There are some longer-chained five-ring compounds which form SmCP_A (in one case a Col_r phase), only. But the majority of the studied six-ring compounds **8** exhibit polymorphism variants with SmCP_A or SmAP_A as well as conventional smectic phases.

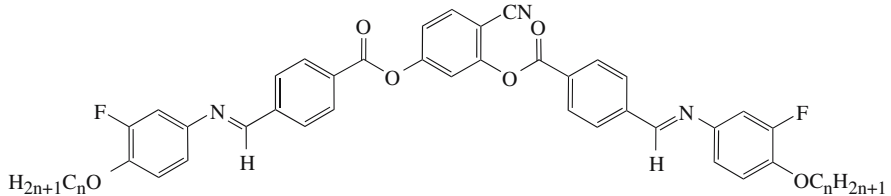


Because the clearing temperatures of the six-ring compounds are rather high, structural investigations and physical measurements are very difficult or impossible, e.g. in some cases SmCP_A and SmAP_A phases could not be distinguished since X-ray studies on oriented samples could not be performed. Depending on the linking groups, on lateral substituents and on the length of the terminal chains following phase sequences with decreasing temperature can occur: $\text{SmA-SmAP}_A/\text{SmCP}_A$; $\text{SmA-SmAP}_A/\text{SmCP}_A\text{-SmA}'$, $\text{SmA-SmA}''\text{-SmCP}_A$; $\text{SmC-SmCP}_A\text{-SmCP}_A'$. The structural differences between SmA and SmA' or SmA'' resp., or between SmCP_A - and SmCP_A' are not yet clear [46].

3. POLYMORPHISM WITH POLAR BIAxIAL SmA PHASES

3.1 SmAP_A Phases Formed by Terminal Non-polar Bent-core Mesogens

The existence of a polar SmA phase formed by bent-core mesogens has been predicted by Brand et al. [47]. For the octyloxy derivative of the following series the SmAP_A phase was experimentally proved for the first time [48].

Table 1-8. Transition temperatures ($^{\circ}\text{C}$) and enthalpy changes [kJ mol^{-1}] of the compounds **9a-9e**


No	n	Cr	SmAP _A	SmA	I			
9a [48]	8	•	73 [74.6]	•	145 [1.2]	•	180.1 [16.7]	•
9b [49]	9	•	78 [30.8]	•	143 [0.4]	•	180 [8.1]	•
9c [49]	10	•	81 [33.7]	•	140 [0.7]	•	183 [8.2]	•
9d [49]	11	•	72 [20.5]	•	137 [0.6]	•	184 [8.1]	•
9e [49]	12	•	75 [18.2]	•	133 [0.7]	•	182 [8.1]	•

As seen from Table 1-8 the SmAP_A phase occurs on cooling the SmA phase. If the SmA phase exhibits a fan-shaped texture this texture does not markedly change at the transition to the SmAP_A phase (Figure 1-9b). Only some irregular stripes parallel to the smectic layers appear on further cooling.

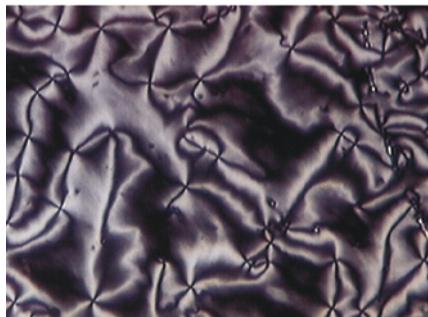
However, if the SmAP_A phase is formed from the homeotropically oriented SmA phase it adopts a strongly fluctuating schlieren texture indicating the biaxial nature of this phase, as shown in Figure 1-9a. The orthogonal alignment of the molecules could be clearly proved by X-ray measurements on an oriented sample. The polar SmA phase shows a current response characteristic for an antiferroelectric ground state. The switching polarization was found to be between 800 and 1000 nCcm⁻² [48, 49].

If the lateral fluorine substituents at the outer rings in the compounds **9** are exchanged by chlorine or bromine also SmAP_A phases occur in the phase sequence SmA-SmAP_A-SmCP_A, see compounds **10** in Table 1-9 [35].

It was found by X-ray diffraction measurements that the layer spacing is nearly the same in all smectic phases. Furthermore the tilt angle of the SmCP_A does not exceed 10°. The strong temperature dependence of the spontaneous polarization is unusual (Figure 1-10).

In comparison to series **9** and **10**, the lateral substituents at the outer rings are missing in the following compounds **11** and the azomethine linking groups are replaced by ester groups, see Table 1-10 [42]. Also in these compounds a SmAP_A phase occurs in the sequence SmA-SmAP_A. The switching polarization (640 and 320 nCcm⁻² for compounds **11a** and **11b**, respectively) is clearly lower than that of the series **9**.

A



B



Figure 1-9. a) Schlieren texture of the SmAP_A phase of compound **9a**; b) Fan-shaped texture of the SmAP_A phase of compound **9a**

Table 1-9. Transition temperatures (°C) of the compounds **10a-10c**

No	n	A	Cr	SmCP _A	SmAP _A	SmA	I				
10a	6	Cl	•	92	•	80	•	120	•	142	•
10b	8	Cl	•	91	•	105	•	117	•	156	•
10c	8	Br	•	89	•	90	•	96	•	146	•

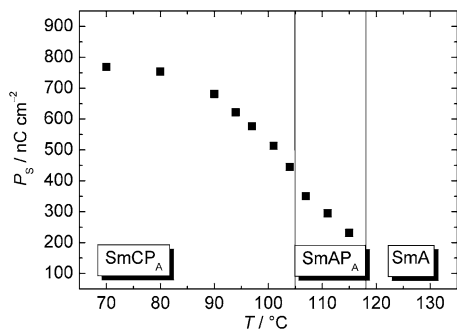


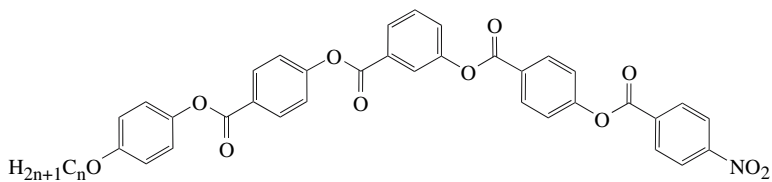
Figure 1-10. Temperature dependence of the switching polarization P_s in the SmAP_A and SmCP_A phase of compound **10b** (reprinted with permission from ref. 35, copyright, 2005, The Royal Society of Chemistry)

Table 1-10. Transition temperatures (°C) and enthalpy changes [$kJmol^{-1}$] of the compounds **11a** and **11b**

No	n	Cr	SmAP _A	SmA	I
11a	8	•	113 [32.4]	• 144 [1.2]	• 187 [8.4]
11b	12	•	106 [16.7]	• 112 [0.9]	• 185 [9.8]

3.2 SmAP_A Phases with a Partial Bilayer Structure (Sm_dP_A) Formed by Terminal Polar Bent-core Mesogens

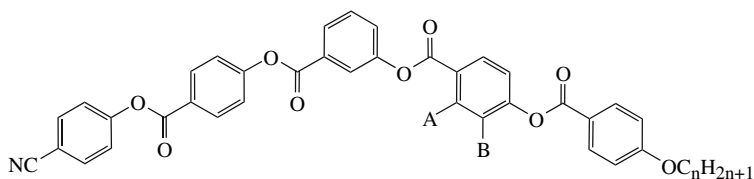
Recently Shreenivasa Murthy et al. [50] have been reported non-symmetric bent-core compounds which contain a nitro group at one end of the molecule



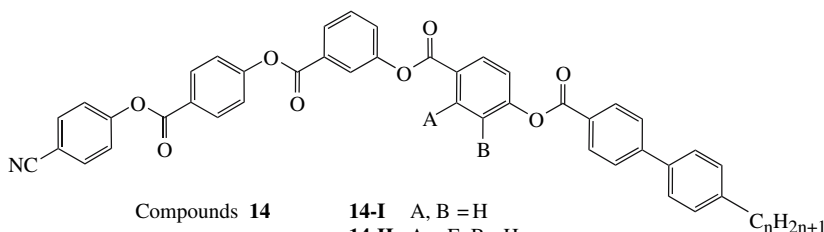
Compounds **12**

The long-chain members of the series **12** ($n = 14, 16, 18$) form two SmA phases the layer spacing of which is significantly larger than the molecular length. This evidently implies a partial bilayer structure of the smectic layers which is also observed in terminal polar calamitic compounds. In contrast to the high-temperature smectic phase (SmA_d) the low-temperature smectic phase is biaxial and shows an antiferroelectric switching; it can be designated as SmA_dP_A.

The same phase sequence SmA_d-SmA_dP_A was found in structurally similar bent-core compounds **13** [51]. In Figure 1-11 the relationship between the length of the terminal chain and the occurrence of this phase sequence is shown for the series **13-I**.

Compounds **13****13-I** A, B = H**13-II** A = F; B = H ($n = 6 \dots 18$)**13-III** A = H; B = F ($n = 6 \dots 18$)

These compounds were synthesized already in 2002 but the polar properties of the low-temperature phase were discovered later [52]. In the terminal polar six-ring bent-core compounds **14** also nematic phases occur.

Compounds **14****14-I** A, B = H**14-II** A = F; B = H**14-III** A = H; B = F

Depending on the length of the terminal chains and the pattern of lateral substitution apart from the dimorphism SmA_d-SmA_dP_A new phase sequences N-SmA_dP_A and N-SmA_d-SmA_dP_A could be detected [52].

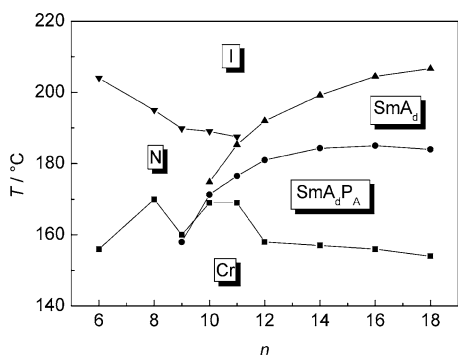
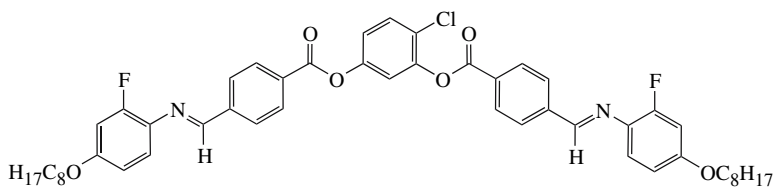


Figure 1-11. Transition temperatures of series **13-I** in dependence on the length of the terminal hydrocarbon chains (reprinted with permission from ref. 52, copyright, 2004, The Royal Society of Chemistry)

4. DIRECT TRANSITIONS FROM THE NEMATIC TO POLAR SMECTIC OR COLUMNAR PHASES

4.1 Direct Transition from the Nematic Phase into the SmCP_A Phase

There are a few bent-core compounds where the polar SmCP_A phase (or another “banana phase”) is directly transformed into a nematic phase. It is plausible that such transitions are not so frequently observed than transitions to non-polar smectic phases since the structural differences are more pronounced. The first examples of a dimorphism SmCP_A-N were reported in 2001 by Weissflog et al. [34] and Amaranatha Reddy et al. [53]. The bent compound described in ref. [34] is derived from 4-chlororesorcinol and possesses fluorine substituents at the outer rings.



15 Cr 71 SmCP_A 99 N 103 I

The only special feature of the nematic phase is the occurrence of cybotactic smectic groups in which the molecules are tilted by 35°.

In ref. [53] three homologous bent-core compounds **16** derived from 2,7-dihydroxynaphthalene are presented which also show the direct transition SmCP_A-N, see Table 1-11.