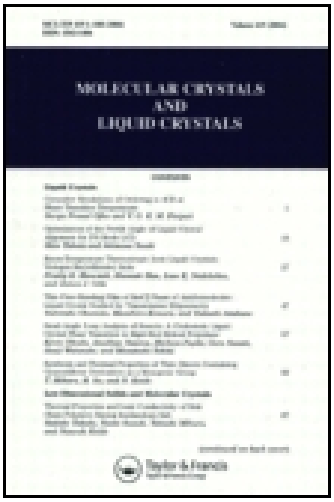

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X-ray and Miscibility Investigations on New Compounds Exhibiting Wide Range Smectic Q Phases

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X-RAY AND MISCIBILITY INVESTIGATIONS ON NEW COMPOUNDS EXHIBITING WIDE RANGE SMECTIC Q PHASES

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Abstract Four new series of liquid crystals are presented. Six of the new chiral compounds which are members of three different series exhibit wide range SmQ phases while their respective racemates and shorter homologues show SmC_A, SmC and SmA phases. X-ray investigations on the SmQ phase of two compounds confirm its three-dimensional tetragonal lattice and show that the lattice parameter c can be both smaller or larger than the parameters a = b.

INTRODUCTION

In 1983 Levelut et al. [1] discovered a new type of liquid crystalline phase which occurs in chiral but not in racemic 1-methylheptylterephthalidene-bis-amino-cinnamate (**MHTAC**). X-ray investigations revealed that this phase, which was denoted as SmQ, has a three-dimensional tetragonal lattice superimposed upon a short range liquid order of the centres of mass. The obtained lattice constants for the SmQ phase of **MHTAC** (a = b = 75.45Å and c = 68.4Å) imply that the unit cell consists of about 350 molecules. However, the arrangement of the molecules within the unit cell could not be determined so far.

Until now no other compound has been reported to possess the SmQ phase. In this contribution we present four new series of chiral liquid crystals and some of their respective racemates: series **1** consists of two higher homologues of **MHTAC**, in series **2** the chiral side chain of **MHTAC** has been varied, in series **3** the Schiff-base groups have

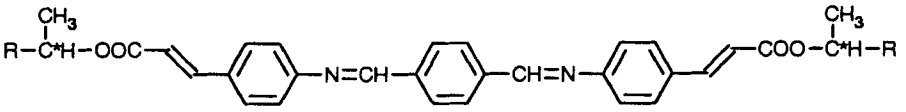
been replaced by ester groups and in series **4** a different mesogenic core has been used. On the basis of textural observations and miscibility studies six chiral compounds are found to exhibit wide range SmQ phases.

The effect of the structural variations as well as the influence of chirality on the occurrence and stability of the SmQ phase is discussed. Moreover, first results of X-ray investigations on the SmQ phase of the new compounds are presented.

EXPERIMENTAL

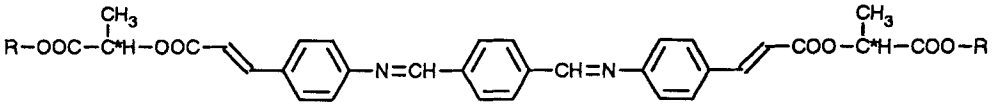
The synthesized new chiral compounds belong to four series (**1** - **4**). Additional to the respective racemates **1a** and **1b** described elsewhere [3] also the racemates **2b**, **2c** and **4b** were prepared. As the racemates were synthesized using the racemic alcohols they consist of (R,R), (S,S), (R,S) and (S,R) enantiomers.

Series **1**:



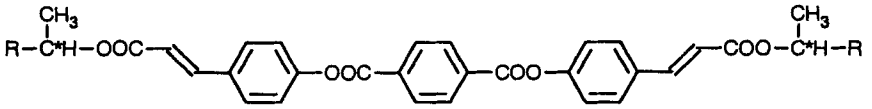
—R = —C_8H_{17} (**1a***), —$C_{10}H_{21}$ (**1b***)

Series **2**:



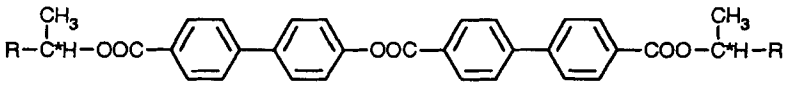
—R = —CH_3 (**2a***), —C_4H_9 (**2b***), —$CH(CH_3)-CH_3$ (**2c***), —$CH(CH_3)-C_2H_5$ (**2d***)

Series **3**:



—R = —C_6H_{13} (**3a***), —COO—C_4H_9 (**3b***)

Series **4**:



—R = —C_4H_9 (**4a***), —C_6H_{13} (**4b***)

The terephthalidene-bis-aminocinnamates of series **1** and **2** were prepared by esterification of 4-nitro-cinnamic acid with the respective chiral or racemic *sec.*-alcohol followed by reduction of the nitro group to amino and condensation of the 4-aminocinnamates with terephthalaldehyde according to descriptions given in [2]. The synthesis schemes of series **3** and **4** are shown in Figure 1 and 2.

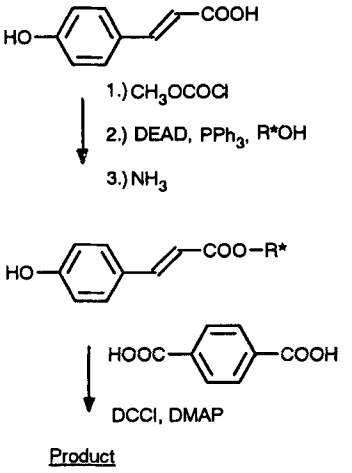


FIGURE 1 Synthesis scheme of series **3**

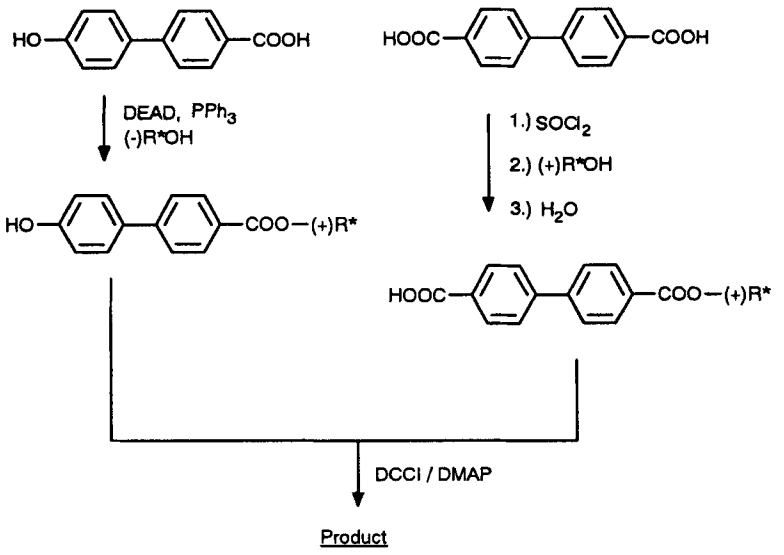


FIGURE 2 Synthesis scheme of series **4**. Note that both enantiomers of the chiral alcohol are needed to get the (R,R) or (S,S) enantiomer of the product.

Transition temperatures were determined optically using a Leitz Ortholux II POL-BK polarizing microscope fitted with a Mettler FP82 heating stage and a Mettler FP80 control unit. Transition enthalpies and melting temperatures were obtained by DSC measurements (heating rate 3K/min) using a Perkin-Elmer DSC 7.

Miscibility studies were carried out by the contact method and, in some cases, in addition, by choosing specific concentrations. For these investigations both enantiomers of **MHTAC** [1] were used as SmQ and SmC_A reference compounds and racemic **M4TAC** [3] for SmC.

X-ray studies were performed in two ways. To assign the lattice, single crystals or partially aligned samples were irradiated by a point focusing X-ray beam (CuKα). Then the lattice parameters were measured with a good accuracy from powder pattern obtained with a Guinier camera ($CuK\alpha_1$). Partially aligned samples - fibres with a common **c** axis - are obtained by heating stacks of crystals into the SmQ phase, while by cooling the isotropic liquid just below the clearing temperature, large single crystal of the mesophase grow slowly.

RESULT

Liquid crystalline properties of the chiral compounds

To study the mesomorphic behaviour of all compounds of the four series textural observations were performed. Three different types of textures are observed[1]: a focal-conic fan texture indicating a SmA phase, a broken focal-conic fan texture typical for SmC or SmC_A phases and a mosaic texture. This mosaic texture (see Figure 3) which appears in six compounds (members of series **1**, **2** and **4**) on cooling from the isotropic phase has rectilinear edges and small birefringence. Other domains of this phase show no birefringence indicating its uniaxiality. A similar texture was reported for a three-dimensional tetragonal mesophase of **MHTAC** denoted as SmQ [1].

In order to classify the different mesophases miscibility studies were carried out with both enantiomers of **MHTAC**. As an example the phase diagram between (S,S)-**MHTAC** and **4b*** is shown in Figure 4. By uninterrupted miscibility the phase sequence K-SmC_A-SmQ-Iso is established for **4b***.

For all other compounds it has been confirmed in the same manner that the phase showing a broken focal-conic fan texture is either a SmC_A or in some cases a SmC phase and the phase showing a mosaic texture is a SmQ phase.

[1]: With the exception of **3b***, see Table III.

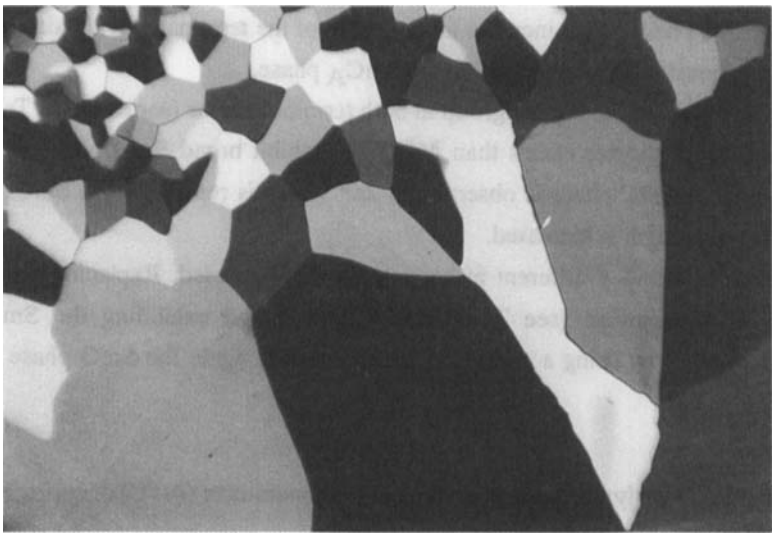


FIGURE 3 Mosaic texture of **4b*** (at 70°C, total scale 2 x 1.3mm²)
See Color Plate XV.

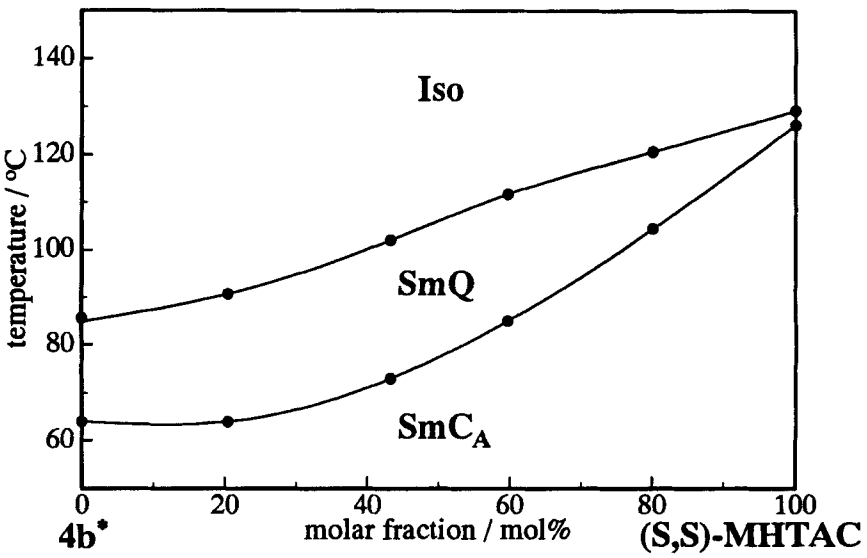


FIGURE 4 Phase diagram of (S,S)-**MHTAC** in **4b***

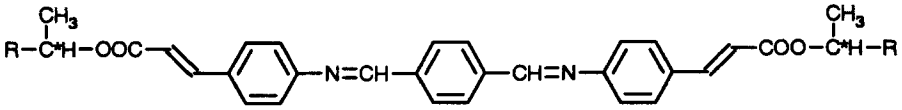
Polymorphism and phase transition temperatures of the chiral compounds under investigation are given in Tables I to IV.

In Table I (series **1**) two higher homologues of chiral **MHTAC** (K 93°C SmC_A 128°C SmQ 131°C Iso) are shown. Whereas shorter homologues of **MHTAC** do not exhibit a SmQ phase [3] an increase in the length of the terminal alkyl chains stabilizes the SmQ phase considerably in respect to the SmC_A phase.

By inserting another ester group in both terminal chains (series **2**, see Table II) even compounds with shorter chains than **MHTAC** exhibit broad SmQ phases ranging from 30K to 50K. A SmC phase is observed in **2a*** which is replaced by a SmQ phase when the alkyl chain length is increased.

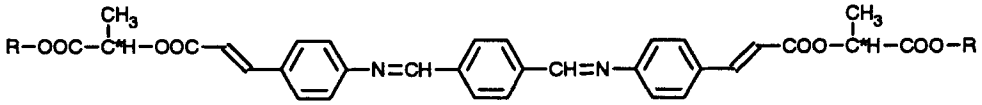
In series **3** and **4** different mesogenic cores were used. Replacing the Schiff-base groups by ester groups (see Table III) no compound exhibiting the SmQ phase is obtained whereas by using a completely different core again the SmQ phase occurs (see Table IV).

TABLE I Polymorphism and transition temperatures (in °C) of series **1**



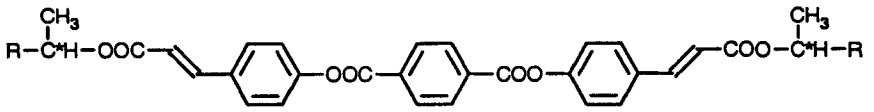
R =	Chirality	K		SmC_A		SmQ		Iso
1a*: $-C_8H_{17}$	(S,S)	•	104	(•	103)	•	128	•
1b*: $-C_{10}H_{21}$	(S,S)	•	94	–		•	118	•

TABLE II Polymorphism and transition temperatures (in °C) of series **2**



R =	Chirality	K		SmC		SmQ		SmA		Iso
2a*: $-CH_3$	(S,S)	•	120	•	210	–		•	253	•
2b*: $-C_4H_9$	(S,S)	•	96	–		•	137	–		•
2c*: $-CH(CH_3)-CH_3$	(S,S)	•	127	–		•	157	–		•
2d*: $-CH(CH_3)-C_2H_5$	(R,R)	•	113	–		•	163	–		•

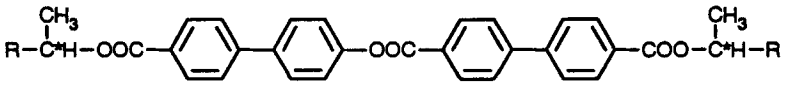
TABLE III Polymorphism and transition temperatures (in °C) of series 3



R =	Chirality	K		SmC_A		SmA		Iso
3a*: —C_6H_{13}	(S,S)	•	139	(•	89)	–		•
3b*[1]: —$COOC_4H_9$	(R,R)	•	43	–	?	•	147	•

[1] Below the SmA phase two unidentified phases were observed both being different from SmQ.

TABLE IV Polymorphism and transition temperatures (in °C) of series 4



R =	Chirality	K		SmC_A		SmQ		Iso
4a*: —C_4H_9	(S,S)	•	44	•	111	–		•
4b*: —C_6H_{13}	(S,S)	•	56	•	60	•	86	•

In all cases the SmQ phase occurs directly below the isotropic phase. The only liquid crystalline phase observed on cooling from the SmQ phase is the SmC_A phase. The values of the transition enthalpies range from 0.2 to 0.7kJ/mol (SmQ-Iso) and from 0.8 to 1.7kJ/mol (SmC_A-SmQ).

Racemic compounds and chiral-racemic phase diagrams

It was shown in [1] that the SmQ phase of **MHTAC** vanishes in chiral-racemic mixtures when the enantiomeric excess is below about 95%. Some of the compounds presented here exhibit more than ten times broader SmQ phase ranges compared to **MHTAC** thus it seemed to be interesting to study the influence of chirality on the occurrence and stability of the SmQ phase of these compounds too. Therefore several racemic compounds have been synthesized (see Table V) and their chiral-racemic phase diagrams have been studied.

As can be seen in Table V the racemates show no SmQ phases but SmC_A or SmC and in some cases additionally SmA phases appear instead. For all racemates a

pronounced increase of the clearing temperature (up to 80K) with respect to the pure enantiomers is found.

TABLE V Polymorphism and transition temperatures (in °C) of racemic compounds.

Compound	K		SmC_A		SmC		SmA		Iso
1a [1]	•	83	•	145	–		–		•
1b [1]	•	79	•	126	–		–		•
2b	•	141	–		•	152	•	213	•
2c	•	187	–		(•	145)	•	203	•
4b [2]	Gl.	-15	•	123	–		•	142	•

[1] Data for **1a** and **1b** are taken from [3].

[2] In **4b** no crystallisation but a glass transition was detected.

In the chiral-racemic phase diagram **4b*-4b** (Figure 5) the SmQ phase exists above 80% and the SmA phase below 40% enantiomeric excess. With increasing enantiomeric excess the clearing temperature is considerably decreased leading to a reduction of the SmC_A temperature range of more than 60K.

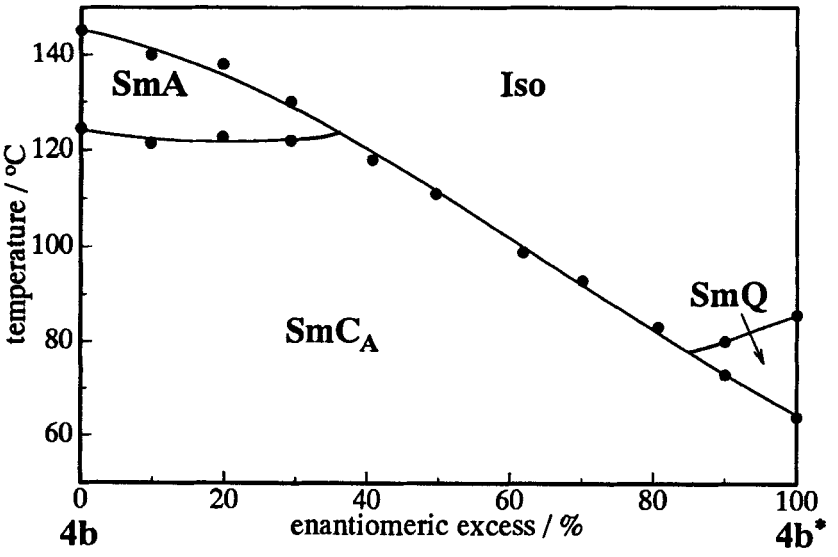


FIGURE 5 Chiral-racemic phase diagram of **4b*** in **4b**

X-ray investigations on the SmQ phase

The structure of the SmQ phase was studied by X-ray investigations. For these studies we used compound **2d*** which has a different chiral side chain and compound **4b*** which has a different mesogenic core than **MHTAC**. Diffraction pattern of partially oriented samples of the SmQ phase confirm a body centred tetragonal lattice superimposed upon a liquid-like order of the centres of mass. The lattice parameters of **2d*** and **4b*** which were calculated from powder pattern were found to be nearly independent of temperature (see Table VI were the lattice parameters of **MHTAC** [1] are included).

TABLE VI Lattice parameters of the tetragonal unit cell of the SmQ phase

Compound	a = b (Å)	c (Å)	c/a
MHTAC [1]	75.45	68.4	0.91
2d*	71.8	120.9	1.68
4b*	73.1	84.15	1.15

[1] Data for **MHTAC** are taken from [1].

For all three compounds the lattice parameters a = b are almost the same whereas the c parameter varies considerably. Note that the c/a ratios can be either smaller or larger than unity. Further X-ray investigations to obtain the lattice parameter of the other SmQ compounds as well as to clarify the structure of this phase are in progress.

SUMMARY

Until now only one compound (**MHTAC**) was known to exhibit the SmQ phase. Starting from the structure of **MHTAC** we have varied the chiral side chains and the mesogenic core which led to the discovery of six new compounds (members of three different series) exhibiting wide range SmQ phases. In shorter homologues of all these series and in racemates the SmQ phase is replaced by SmC_A or in some cases by SmC phase. Additionally, in the investigated systems chirality leads to a remarkable strong decrease of the clearing temperature.

X-ray investigations on the SmQ phase have shown that the lattice parameters of the tetragonal unit cell are almost independent of temperature and the ratio c/a of the lattice parameters can be either smaller or larger than unity.

Our observations indicate that the SmQ phase is induced by chirality. Furthermore, this phase seems to occur preferably in long chain members of antiferroelectric liquid

crystals. It is interesting to note that all known SmQ compounds possess two chiral side chains and an almost symmetrical molecular structure. The only slightly non symmetrical SmQ compound **4b*** offers the possibility to vary both side chains (especially their chirality) independently in order to study the molecular prerequisites for the formation of the SmQ phase. Such work is in progress.

ACKNOWLEDGEMENT

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