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New Heterocyclic Core Structure for Chiral Liquid Crystals

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The synthesis of a new heterocyclic core has been developed. Its standard derivatives afforded new types of FLCs and their physical properties were determined.

Keywords: heterocyclic FLC; synthesis; mesomorphic properties

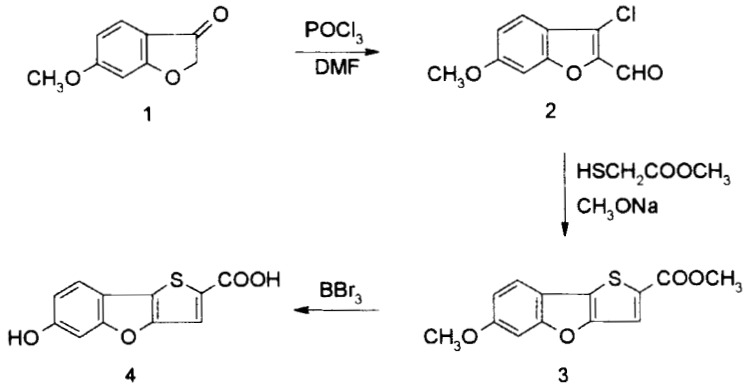
INTRODUCTION

In 1975 it was suggested that ferroelectricity could arise in tilted smectic phases of chiral molecules. This claim was experimentally confirmed a year later and from that time plenty of FLCs have been synthesized[1]. The reasons for the introduction of heterocyclic nuclei into the molecules of FLCs are numerous. The heterocycle can in principle influence the polarisation and polarisability as well as the shape of the molecule which in turn change the type of mesophase, phase transition temperatures and dielectric properties[2,3]. Recently[4] we have developed a new and versatile

synthesis of thieno[3,2-b]benzofuran. The aim of this work is to incorporate this heterocyclic nucleus into structures usually possessing FLC properties.

SYNTHESIS

The heterocyclic core was prepared in a modified route leading to unsubstituted thieno[3,2-b]benzofuran[4]. The starting 6-methoxy-benzo[b]furan-3(*2H*)-one[5] (**1**) underwent a Vilsmeier-Haack formylation with phosphorus oxychloride and N,N-dimethylformamide (DMF) and afforded 3-chloro-6-methoxybenzo[b]furan-2-carboxaldehyde (**2**) (Scheme 1).

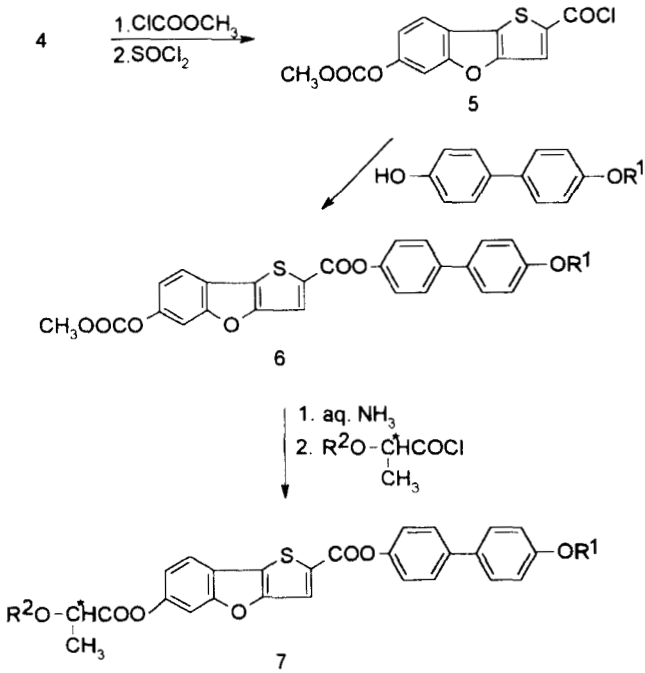


Scheme 1

Nucleophilic substitution of chlorine atom in aldehyde **2** with methyl thioglycolate in basic media was followed by a spontaneous cyclisation of the intermediate to methyl 6-methoxythieno[3,2-b]benzofuran-2-carboxylate (**3**). Both ether and ester groups of **3** were deprotected in a one-pot procedure by treatment with boron tribromide in dichloromethane

to give 6-hydroxythieno[3,2-b] benzofuran-2-carboxylic acid (**4**) as the new heterocyclic core.

Synthesis of series of FLC is described in Scheme 2. First of all the 6-hydroxy group in acid **4** was protected by acylation with methyl chloro-



Scheme 2

formate in pyridine and the carboxylic acid functionality was then transformed to the corresponding 6-[(methoxycarbonyl)oxy]thieno[3,2-b]benzofuran-2-carbonyl chloride (**5**). The chloride **5** was treated with a series of 4-n-alkyl-4′-hydroxybiphenyls (R^1 = n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$) in pyridine to give rise to esters **6**. The hydroxy group of **6** was then deprotected with aq. ammonia in 1,2-dichloroethane. Acylation with a

series of (S)-2-alkoxypropanonyl chlorides (R^2 = n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$) in pyridine afforded a series of new compounds **7**.

RESULTS AND DISCUSSION

Phase transition temperatures were determined using a Perkin Elmer 7 differential scanning calorimeter and by a Amplival Pol polarizing microscope with a hot stage (5 and 10 °C/min temperature gradient).

TABLE 1 Transition temperatures of compounds **7**

Compound	R^1 / R^2	Transition temperature °C									
		C		SmC*		N*		BP		I	
7a	n-C_8H_{17} / n-C_6H_{13}	•	123	•	225	•	233	•	234	•	
7b	n-$_{10}H_{21}$ / n-C_6H_{13}	•	119	•	215	•	220	•	224	•	
7c	n-$_{12}H_{25}$ / n-C_6H_{13}	•	114	•		-		-	213	•	
7d	n-C_8H_{17} / n-C_8H_{17}	•	122	•	220	•	225	•	227	•	
7e	n-$_{10}H_{21}$ / n-C_8H_{17}	•	112	•	215	•	217	•	218	•	
7f	n-$_{12}H_{25}$ / n-C_8H_{17}	•	119	•		-		-	217	•	
7g	n-C_8H_{17} / n-$_{10}H_{21}$	•	120	•	213	•	215	•	217	•	
7h	n-$_{10}H_{21}$ / n-$_{10}H_{21}$	•	120	•		-		-	214	•	
7i	n-$C_{12}H_{25}$ / n-$C_{10}H_{21}$	•	118	•		-		-	208	•	
7j	n-C_8H_{17} / n-$_{12}H_{25}$	•	121	•		-		-	211	•	
7k	n-$_{10}H_{21}$ / n-$_{12}H_{25}$	•	117	•		-		-	207	•	
7l	n-$C_{12}H_{25}$ / n-$C_{12}H_{25}$	•	117	•		-		-	199	•	

The transition temperatures of the series of compounds **7** are shown in TABLE 1. All the synthesised new LCs formed a smectic C* phase (SmC*) (see FIGURE 1) in a very broad temperature interval approx. 100 °C. In addition, some of the crystals (**7a**, **7b**, **7d**, **7e**, **7g**) have also shown a narrow cholesteric (N*) (FIGURE 2) and an extraordinary broad (up to 4 °C) blue phase (BP) (FIGURE 3 and 4).

In the SmC* phase the spontaneous polarisation (Ps) was measured. The measurement was prevented near the high temperature limit of this phase by high conductivity resulting from slow decomposition. At low temperatures Ps could not be measured due to high switching field (which increased gradually with decreasing temperature). For compounds **7a** – **7c** and **7g** Ps could not be determined in any temperature. In Table 2 the values of Ps are shown for the limits of the temperature interval , where Ps was measurable. Generally, the values of Ps are relatively high and increase with decreasing temperature.

TABLE 2 Spontaneous polarisation of compounds **7**

Compound		Spontaneous polarisation[a]/Temperature			
	R^1 / R^2	P_S nC.cm^{-2}	°C	P_S nC.cm^{-2}	°C
7d	n-C_8H_{17} / n-C_8H_{17}	88	172	115	130
7e	n-$C_{10}H_{21}$ / n-C_8H_{17}	82	172	-	-
7f	n-$C_{12}H_{25}$ / n-C_8H_{17}	32	208	44	140
7h	n-$C_{10}H_{21}$ / n-$C_{10}H_{21}$	52	213	107	130
7i	n-$C_{12}H_{25}$ / n-$C_{10}H_{21}$	51	207	57	120
7j	n-C_8H_{17} / n-$C_{12}H_{25}$	40	210	82	130
7k	n-$C_{10}H_{21}$ / n-$C_{12}H_{25}$	2	195	-	-
7l	n-$C_{12}H_{25}$ / n-$C_{12}H_{25}$	88	130	-	-

[a] at 60 Hz and 50 V

FIGURE 1 Smectic C^* phase of compound **7b** in the polarizing microscope (214 °C) (See color plate XIX at the back of this issue)

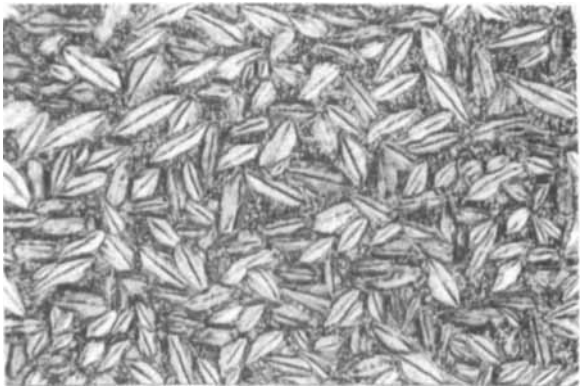


FIGURE 2 Cholesteric N^* to smectic C^* phase transition of compound **7b** (215 °C) (See color plate XX at the back of this issue)

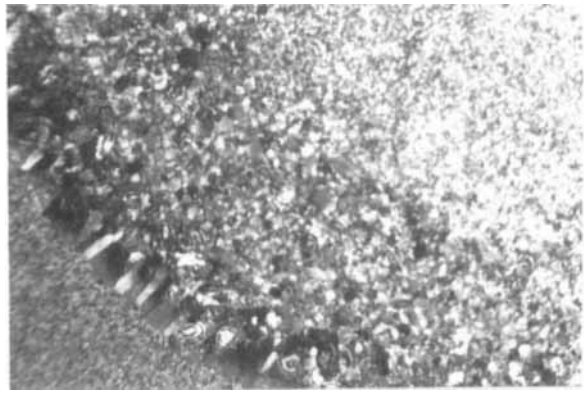


FIGURE 3 Blue to cholesteric N^* phase transition of compound **7b** (220 °C)
(See color plate XXI at the back of this issue)

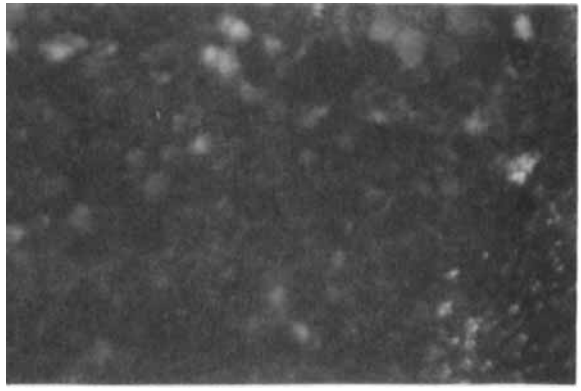


FIGURE 4 Blue phase (BP) of compound **7d** (226 °C)
(See color plate XXII at the back of this issue)

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