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## Liquid Crystals

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# Synthesis and liquid crystal properties of new banana-shaped cinnamoyl derivatives

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Three new achiral five-ring banana-shaped homologous series have been synthesized and their liquid crystalline properties studied by polarizing microscopy, differential scanning calorimetry, and electro-optical analysis. The compounds consist of two identical mesogenic structures of bis(alkoxycinnamoyloxybenzoates) linked on a different central ring (unsubstituted or methyl-substituted). The length of the terminal alkoxy groups was varied from heptyloxy to dodecyloxy; the hexadecyloxy group was also included in the study. It was found that the polymorphism of compounds can be strongly dependent upon molecular structure in this class of compound. In particular, substituents on the central ring may exert a significant effect on the type of mesophase observed.

## 1. Introduction

The influence of molecular chirality on mesophase behaviour and macroscopic structure is of major interest in liquid crystal research. From this point of view, the chirality of the whole material is important. In 1996 Niori [1] reported the ferroelectric switching of a liquid crystalline phase ( $B_2$ ) formed by bent core achiral molecules, so-called banana-shaped molecules. To understand the structure of this mesophase many investigations have been reported [2–4]. The novel electro-optical behaviour of the  $B_2$  phase is based on macroscopic phase structure rather than molecular chirality. In the case of this new ferroelectric phase, molecular packing is the determining feature. This new polymorphism has been typically observed and thoroughly investigated for 1,3-disubstituted benzene derivatives, each substituent of which characteristically possesses two additional 1,4-disubstituted phenyl groups connected by a Schiff' base moiety [5–8].

The aim of the present work was to synthesize novel compounds which incorporate the typical 1,3-disubstituted benzene central unit but with additional phenyl groups connected by  $-C=C-COO-$  moieties instead of the more usual  $-C=N-$  groups. We expected that these compounds would exhibit improved liquid crystalline properties, being geometrically closely related to known banana-shaped molecules, yet differing significantly from those compounds in their chemical structures. For this purpose,

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the introduction of *p*-alkoxycinnamoyl groups seemed to be particularly economic and straightforward [9]. Study of structure–property relationships in this novel class of compounds was also thought to be an interesting aspect of our work and to this end, we report the synthesis and characterization of a range of five-ring (aromatic rings) compounds with various substituents in different positions.

## 2. Experimental

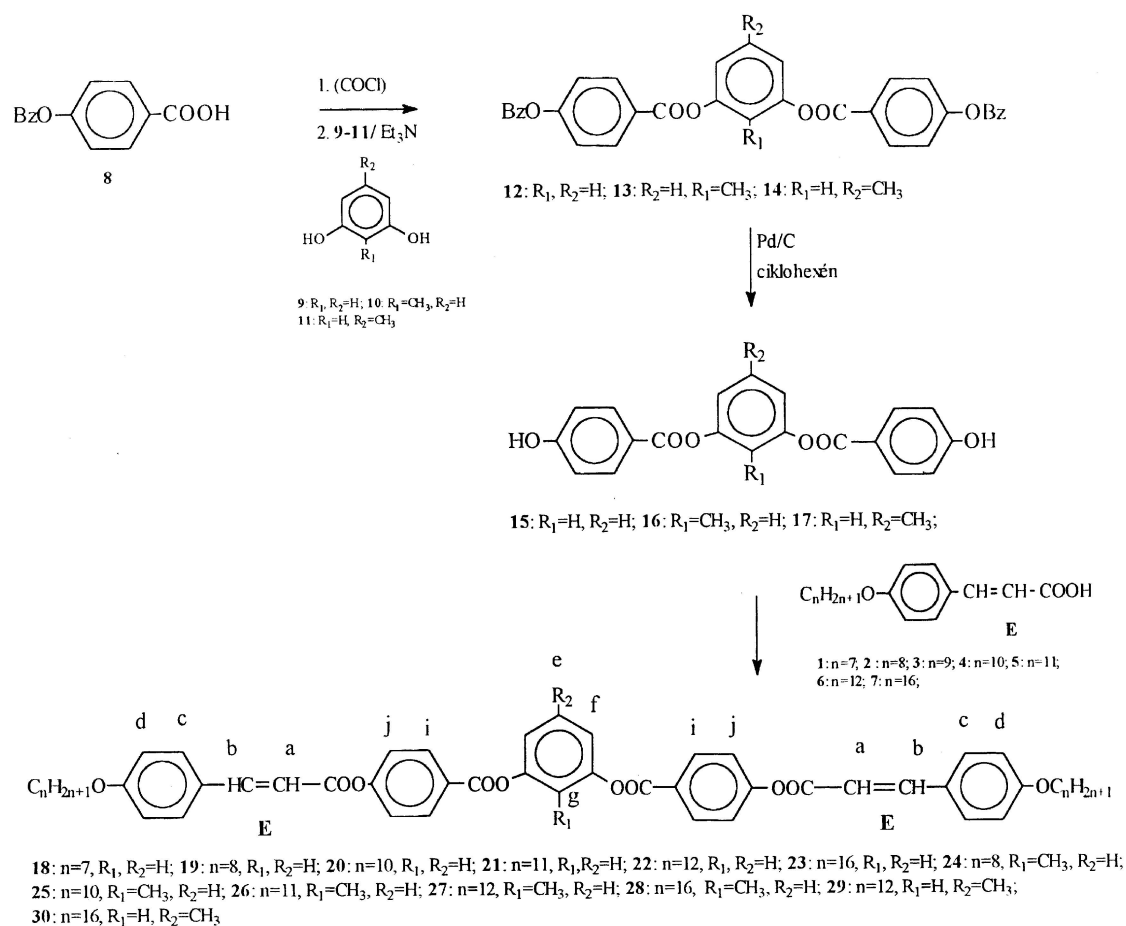
### 2.1. Synthesis

Reagents were purchased from commercial suppliers and used as received; solvents were dried and distilled before use. For column chromatography, Kieselgel 60 (0.063–0.02 mm) (Merck) was used, and eluted with chloroform. Organic extracts were dried over anhydrous magnesium sulfate.

The alkoxycinnamic acids 1–7 [10] and 4-benzyloxybenzoic acid [11] were synthesized according to procedures described in the literature. The syntheses of the new five-ring compounds 18–30 were achieved as shown in scheme 1; details are given below.

#### 2.1.1. Preparation of 4-benzyloxybenzoyl chloride

4-Benzyloxybenzoic acid (3 g, 13 mmol) was dissolved in dry dioxane (5 cm<sup>3</sup>), and oxalyl chloride (23 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. The unreacted oxalyl chloride was removed under vacuum, and the crude product obtained was used in the next step without further purification.



Scheme 1. Synthetic route for five-ring banana-shaped liquid crystals.

### 2.1.2. Preparation of acylated resorcinol or monosubstituted resorcinols (12–14)

Crude 4-benzyloxybenzoyl chloride (12.1 g, 49 mmol) was dissolved in dry dioxane (202 cm<sup>3</sup>). To this solution, either resorcinol, 2-methylresorcinol or 5-methylresorcinol (24 mmol), and then triethylamine (8.4 cm<sup>3</sup>) were added. The mixture was agitated at room temperature for 4 h, then the solvent was evaporated under vacuum. The solid residue was dissolved in chloroform and the solution extracted with water (4 × 50 cm<sup>3</sup>). The organic phase was dried over anhydrous magnesium sulfate, and the solvent evaporated under vacuum. The crude product was recrystallized from ethyl acetate to obtain the acylated resorcinol (12–14). Average yield 84.3%; m.p. 13 162°C; 14 156°C.

### 2.1.3. Debenzylation of compounds 12–14 to give 15–17

Compound 12, 13 or 14 (1.88 mmol) was dissolved in hot ethanol (10 cm<sup>3</sup>), and to the solution cyclohexene (3 cm<sup>3</sup>) and Pd/C catalyst (10%, 0.1 g) were added. The mixture was stirred at 50°C for 6 h. The catalyst was filtered off, and the filtrate evaporated under vacuum to

give the pure product as a white solid powder in quantitative yield (98%). M.p. 15 248°C; 16 221°C; 17 230°C [12].

### 2.1.4. Acylation of intermediates 15–17 to give compounds 18–30

An alkoxyacrylate (1–7) (3.38 mmol) was dissolved in anhydrous dioxane (20 cm<sup>3</sup>). To this solution, one of compounds 15–17 (1.30 mmol) and triethylamine (3.38 mmol) were added. The suspension was agitated at room temperature for 20 h. The solvent was removed under vacuum, and the residue washed with water, dried and recrystallized from isopropanol or purified by column chromatography.

## 2.2. Characterization

### 2.2.1. Structure determination

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at ambient temperature in CDCl<sub>3</sub>, using the <sup>2</sup>H signal of the solvent as the lock, and tetramethylsilane as the internal standard. A Bruker AM (at 200 MHz) spectrometer was used. Coupling constants *J* are given in Hz.

Table 1.  $^1\text{H}$  NMR data for compounds **18–30**.

Compound	$\text{CH}_3$ t	$\text{OCH}_2\text{CH}_2$ q, 4H	$\text{OCH}_2$ t, 4H	$\text{CH}^a$ d, 2H	$\text{CH}^b$ d, 2H	$\text{CH}^c$ d, 4H	$\text{CH}^d$ d, 4H	$\text{CH}^{e\ddagger}$ 1H	$\text{CH}^{\text{ff}}$ 1H	$\text{CH}^{\text{g}\ddagger}$ 1H	$\text{CH}^i$ d, 4H	$\text{CH}^j$ d, 4H
<b>18</b>	0.90	1.95	4.00	6.49	7.86	7.54	6.93	7.46–7.57	7.15–7.20	—	8.26	7.34
<b>19</b>	0.90	1.81	4.00	6.49	7.86	7.51	6.93	7.47–7.53	7.15–7.20	—	8.26	7.32
<b>20</b>	0.87	1.79	4.00	6.49	7.86	7.50	6.93	7.46–7.57	7.16–7.19	—	8.26	7.34
<b>21</b>	0.89	1.78	4.02	6.50	7.87	7.51	6.93	7.37–7.57	7.17–7.20	—	8.27	7.30
<b>22</b>	0.88	1.81	4.00	6.49	7.86	7.50	6.93	7.45–7.52	7.15–7.20	—	8.26	7.34
<b>23</b>	0.88	1.80	4.00	6.49	7.87	7.51	6.93	7.49–7.57	7.15–7.19	—	8.27	7.33
<b>24</b> <sup>†</sup>	0.90	1.79	4.00	6.50	7.86	7.55	6.93	~7.30	7.13	—	8.27	7.31
<b>25</b> <sup>†</sup>	0.88	1.83	4.00	6.50	7.86	7.53	6.93	~7.32	7.13	—	8.29	7.32
<b>26</b> <sup>†</sup>	0.88	1.79	4.00	6.49	7.86	7.54	6.93	~7.29	7.12	—	8.28	7.29
<b>27</b> <sup>†</sup>	0.88	1.79	4.00	6.50	7.86	7.55	6.93	~7.31	7.13	—	8.30	7.31
<b>28</b> <sup>†</sup>	0.88	1.79	4.00	6.50	7.86	7.55	6.93	~7.32	7.13	—	8.29	7.32
<b>29</b> <sup>‡</sup>	0.88	1.82	4.00	6.59	7.86	7.54	6.93	—	6.98	—	8.23	7.31
<b>30</b> <sup>‡</sup>	0.88	1.81	4.00	6.49	7.86	7.55	6.93	—	6.98	—	8.25	7.33

Coupling constants (Hz): **18–23**  $J_{a,b} = 16.5$ ,  $J_{c,d} = 8.8$ ,  $J_{i,j} = 8.8$ ; **24–28**  $J_{a,b} = 16.0$ ,  $J_{c,d} = 8.8$ ,  $J_{f,g} = 8.0$ ,  $J_{i,j} = 8.8$ ; **29–30**  $J_{a,b} = 16.0$ ,  $J_{c,d} = 8.8$ ,  $J_{i,j} = 8.8$ . Multiplicity in **18–23**: m ( $\text{CH}^e$ ), m ( $\text{CH}^f$ ), m ( $\text{CH}^g$ ); in **24–28**: d ( $\text{CH}^f$ ), m ( $\text{CH}^g$ ); in **29–30**: s ( $\text{CH}^f$ ), m ( $\text{CH}^g$ ).

<sup>†</sup> The 2- $\text{CH}_3$  group sign: 2, 11 (s, 3H) ppm

<sup>‡</sup> The 5- $\text{CH}_3$  group sign: 2, 43 (s, 3H) ppm

Spectral data are listed in table 1. All the spectra were recorded at the Department of Organic Chemistry at Semmelweis University (Budapest).

### 2.3. Optical and thermodynamic properties

All transition temperatures and the textures of the mesophases were identified using a PHMK 80/2914 polarizing microscope equipped with a Boetius hot stage. Transition temperatures were confirmed using a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated with indium. The heating and cooling rates were 5 or  $2^\circ\text{C min}^{-1}$ . Non-oriented samples of compounds with liquid crystal properties were studied using X-ray diffraction.

## 3. Results and discussion

### 3.1. Synthesis

By changing the central core and the length of the terminal chains, we prepared thirteen five-ring banana-shaped molecules (scheme 2) and examined the effects of chemical structure on the liquid crystal mesophases.

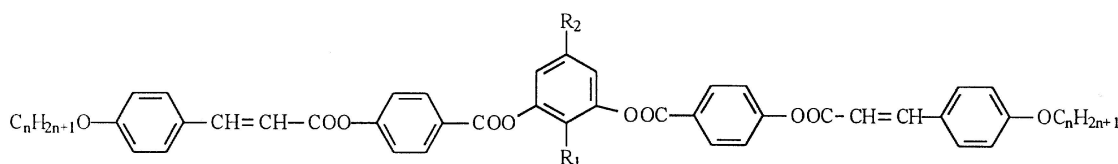
The syntheses of the new five-ring compounds **18–30** were achieved as shown in scheme 1. The five-ring compounds were obtained from *p*-benzyloxybenzoic acid **8** and resorcinol **9**, 2-methylresorcinol **10** or 5-methylresorcinol **11**, in three steps: (a) acylation of resorcinol or

methyl-substituted resorcinol with the protected benzoic acid; (b) removal of the protecting group, and (c) acylation of the 1,3-phenylene bis(4-hydroxybenzoate) or substituted 1,3-phenylene bis(4-hydroxybenzoate), with alkoxybenzoic acid (scheme 2). The structures of all compounds were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance.

### 3.2. Thermal and liquid crystalline properties

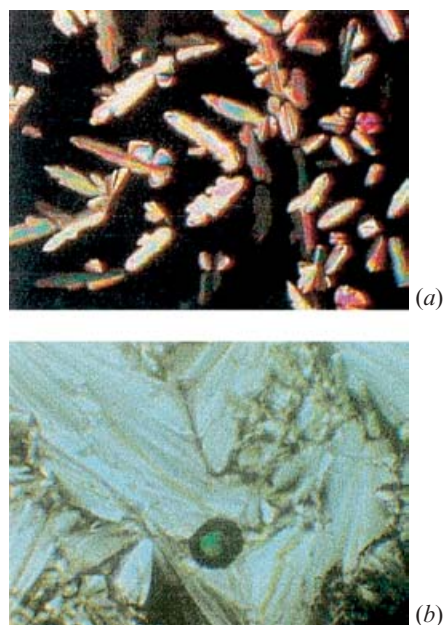
The mesophase behaviour and electro-optic properties of the new five-ring compounds **18–30** were investigated. Mesophase identification was based on microscopic examination of the liquid crystalline textures, and X-ray and DSC measurements. Those compounds which exhibit mesophases, were investigated under an applied electric field.

The resorcinol derivatives **18–23** show various mesophasic behaviour. **18** and **19** exhibit an enantiotropic  $B_1$  mesophase, **20–22** are not liquid crystalline while **23** has a rich polymorphism. Thus, the liquid crystal properties of this homologous series are very sensitive to changes in the length of the terminal chains. On heating, the  $B_1$  phase of the heptyloxy (**18**) and octyloxy (**19**) resorcinol derivatives grows as dendritic nuclei, which coalesce to give a fan-like texture (figure 1). At the clearing point they become isotropic liquids (table 2).



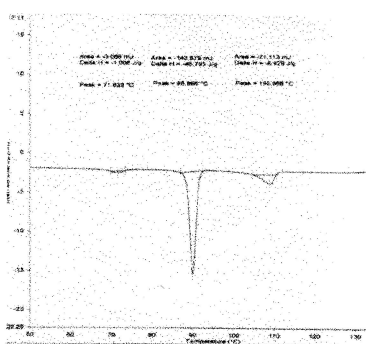
Scheme 2. **18–23**:  $R_1, R_2 = \text{H}$ ,  $n = 7, 8, 10, 11, 12, 16$ ; **24–28**:  $R_1 = \text{CH}_3$ ,  $R_2 = \text{H}$ ,  $n = 8, 10, 11, 12, 16$ ; **29–30**:  $R_1 = \text{H}$ ,  $R_2 = \text{CH}_3$ ,  $n = 12, 16$ .



Figure 1.  $B_1$  phase at different magnifications.Table 2. Phase sequences and transition temperatures ( $^{\circ}\text{C}$ ) of resorcinol derivatives **18–23**.

Compound	$n$	Cr	$B_5$	$B_6$	$B_1$	I
<b>18</b>	7	•	130	—	•	147 •
<b>19</b>	8	•	117	—	•	130 •
<b>20</b>	10	•	122	—	—	•
<b>21</b>	11	•	121	—	—	•
<b>22</b>	12	•	118	—	—	•
<b>23</b>	16	•	108	•	113 •	127 — •

Compound **23** has a  $B_5$  phase over the narrow temperature range from 108 to  $113^{\circ}\text{C}$ . The transition is accompanied by a small transition enthalpy ( $1.495 \text{ J g}^{-1}$ ) (figure 2), but by a significant textural change. An electro-optic response could only be detected close to the  $B_5 \rightarrow B_6$  transition temperature. The  $B_6 \rightarrow B_5$  transition is accompanied by a change in the X-ray pattern (non-oriented sample) in the wide angle region.

Figure 2. DSC thermogram of compound **23** on heating.

On increasing the temperature of **23** a smooth fan-shaped texture appears (figure 3), which might indicate the formation of a  $B_2$  phase. Electro-optic investigations, however, ruled out this possibility. Although the sample responded to the application of electric fields, this response was independent of the polarity. With increasing voltage, stripes parallel to the smectic layers did not occur. Moreover, no current peaks were detected when a triangular voltage (80 V peak to peak) was applied. These observations indicate that this mesophase does not exhibit a macroscopic spontaneous polarization. From these observations we concluded that compound **23** exhibits a  $B_6$  (or SmC) phase rather than a  $B_2$  phase. The experimental data of the homologous series **18–23** are summarized in table 2.

On changing the structure of the central core,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{H}$  (scheme 2), only two molecules (**27**, **28**) can form liquid crystal phases. The compounds **24–26** of the 2-methylresorcinol-based homologous series are not liquid crystalline. On increasing the length of the terminal chains a monotropic  $B_6$  phase appears at the dodecyloxy derivative and becomes an enantiotropic phase in the case of the hexadecyloxy derivative (table 3). The textures of the compounds are quite similar and show a homeotropic Schlieren texture on cooling (figure 4). The phase transitions of these compounds observed under the microscope were confirmed by DSC analysis.

Figure 3.  $B_6$  mesophase of compound **23**.Table 3. Phase sequences and transition temperatures ( $^{\circ}\text{C}$ ) of 2-methylresorcinol (**24–28**) and 5-methylresorcinol (**29–30**) derivatives.

Compound	$n$	$\text{CH}_3$	Cr	$B_3$	$B_6$	I
<b>24</b>	8	$R_1$	•	152	—	— •
<b>25</b>	10	$R_1$	•	129	—	— •
<b>26</b>	11	$R_1$	•	127	—	— •
<b>27</b>	12	$R_1$	•	115	—	• (84) •
<b>28</b>	16	$R_1$	•	95	—	• 130 •
<b>29</b>	12	$R_2$	•	83	•	130 • 145 •
<b>30</b>	16	$R_2$	•	99	•	(102) — •

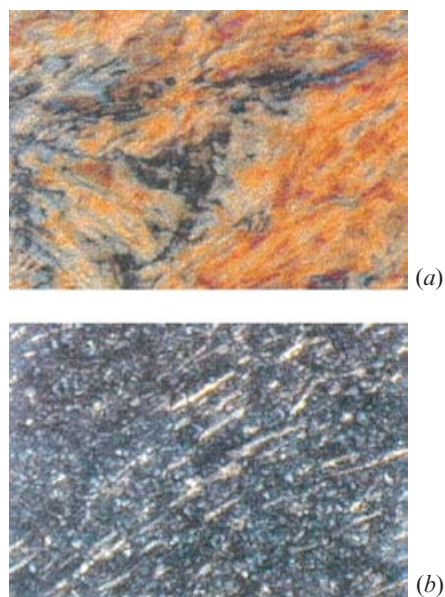


Figure 4.  $B_6$  mesophase of compound **28** on heating (a) and cooling (b).

An examination of the liquid crystal properties of these compounds shows that longer alkoxy tails lead to enantiotropic liquid crystal phases whereas shorter tails result in monotropic phases. Comparing the phase sequences of the resorcinol- and 2-methylresorcinol-based compounds we may conclude that by changing the structure of the central core different mesophase behaviour appears.

By changing the position of the  $\text{CH}_3$  group on the central core two compounds (**29**, **30**) were synthesized. Compound **29** was found to exhibit enantiotropic  $B_3$  and  $B_6$  phases over a wide range of temperatures. On cooling from the isotropic liquid the  $B_6$  phase was assigned on the basis of the Schlieren texture in which homocentric circle domains could be seen; see figure 5 (a). The structure of these domains could be the result of molecular packing. At the transition to the  $B_3$  phase a very clear textural change could be seen. The striped

domains disappear and smooth, well-defined domains appear which were frozen in at the freezing temperature; see figures 5 (b), and 5 (c).

The DSC analysis revealed three endothermic peaks suggesting that the compound has two mesophases and is an enantiotropic liquid crystal. On elongating the alkoxy chains (**30**) a monotropic mesophase appears over a very narrow temperature interval (table 3). The X-ray measurements for a non-oriented sample display strong distinct reflections in the wide angle region, which suggest a crystalline,  $B_3$  phase. This observation is in contrast to our earlier observation because in this homologous series the stability of mesophases decreased on increasing the chain length.

#### 4. Concluding remarks

Three homologous series derived from alkoxybenzoic acid were synthesized. The members of the 1,3-phenylene bis(4-alkoxycinnamoyloxy)benzoate series showed the greatest ability to form less viscous mesophases. The heptyloxy and octyloxy resorcinol derivatives do have  $B_1$  mesophases, whereas the decyloxy, undecyloxy and dodecyloxy compounds do not exhibit liquid crystalline properties. Two mesophases, the  $B_6$  and  $B_3$  phases, are stabilized in the case of the hexadecyloxy derivative.

The change of substituents on the central 1,3-phenylene unit has generally been a successful approach to create new banana-shaped mesogens. We also identified a new polymorphism in substances bearing a methyl group in the 2- or 5-position of the central benzene ring. The 2-methylresorcinols with short alkoxy substituents are crystalline solids exhibiting no mesomorphic properties. On increasing, the terminal chain lengths, however, mesomorphic behaviour appears; the dodecyloxy derivative has a monotropic  $B_6$  phase and the hexadecyloxy derivative has an enantiotropic  $B_6$  phase. In the case of the 5-methyl derivatives, a new phase, namely the  $B_3$ -phase, could be detected, interestingly, the stability of this phase decreased with increasing terminal chain length.

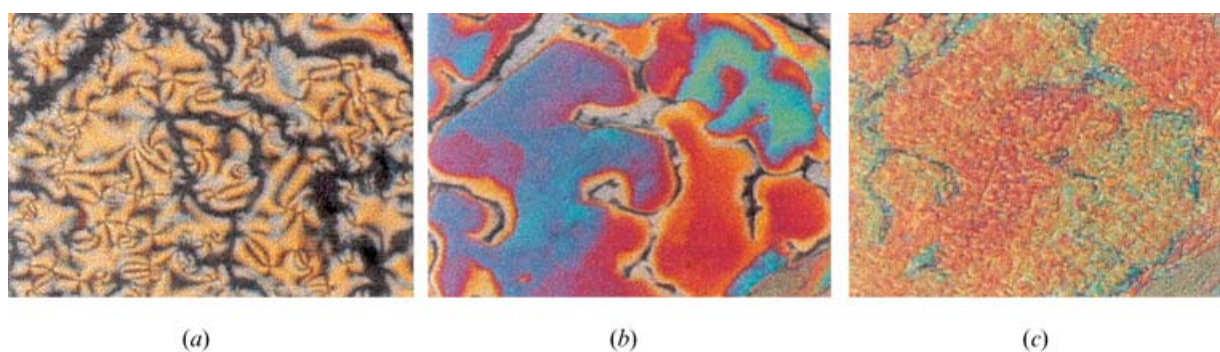


Figure 5. Textures of  $B_6$  (a),  $B_3$  (b), Cr (c) of compound **29**.

All these results clearly indicate that liquid crystalline properties may be strongly dependent upon molecular structure in this class of compounds. In particular, substituents on the central ring may exert a significant effect on the type of mesophase observed, whereas the tendency to exhibit liquid crystallinity can be strongly influenced by the structure of the mesogen moiety. In addition, liquid crystalline properties may also be modified by the terminal alkyloxy chains, and in many cases an optimal length can be found.

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