Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Chiral liquid crystalline compounds with a re-entrant SmA* phase

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Synthesis of studied compounds

We have synthesized new compounds consisting of two biphenyls connected by an ester group, one biphenyl being laterally substituted by chlorine atom. The chiral part contains two chiral centres: methyl-buthyl and lactate group. We have varied the length of the non-chiral chain by changing the number of carbon atoms, *n*, in an alkyl chain C_nH_{2n+1}. Compounds have been designated as **nZBL**. The synthesis of the compounds studied was carried out according to the synthetic path described in following Scheme ESI. Both chiral centres have the (S) configuration.

Preparation of (S)-2-methylbutyl-(S)-lactate 1

A solution of 100 g (S)-lactic acid (Lachema) and 0,8 mol (S)-2-methylbutanol (Merck) in 300 ml of benzene was refluxed using Dean and Stark trap for 25 hours. Benzene was evaporated and the residue was filtered and distilled in vacuum, the first fraction being 2-methylbutanol, the second one being (S)-2-methylbutyl-(S)-lactate ($[\alpha]^{20}_D$ = -10,5° neat).

^{1}H-NMR of 1 ($CDCl_3$, 300 MHz,):

4.25 (q, 1H, CHOH); 4.0 (m, 2H, $COOCH_2$); 3.3 (brs, 1H, OH); 1.7 (m, 1H, CH_2CH*); 1.38 (d, 3H, CH_3CHOH); 1.2 and 1.4 (m, 2H, CH_2CH_3); 0.9 (m, 6H, 2 x CH_3).

Preparation of acid 2

The 4-methoxybiphenyl was chlorinated by sulphuryl chloride during boiling for one hour. The 3-chloro-4-methoxybiphenyl was reacted with acetic acid chloride in presence of aluminium chloride in dichloroethane solution. Resulting acetophenone derivative was converted into acid 2 by the haloform reaction with total yield about 60 percent.

^{1}H-NMR of 2 (DMSO, 300 MHz,):

7.95 (d, 2H, ortho to -COOH); 7.80 (d, 2H, meta to -COOH); 7.78 (d, 1H, ortho to –Cl); 7.7 (dd, 1H, para to –Cl); 7.25 (d, 1H, meta to -Cl); 3.90 (s, 3H, CH_3O).

Preparation of 4-hydroxy-3-chlorobiphenyl-4´-carboxylic acid 3

Methyl group of acid 2 was removed by boiling in hydrobromic acid/acetic acid mixture for several days. Then the reaction mixture was cooled down and poured into water. Resulting 4-hydroxy-3-chlorobiphenyl-4´-carboxylic acid (3) was separated as a yellow powder by suction.

^{1}H-NMR of 3 (DMSO, 300 MHz):

7.95 (d, 2H, ortho to -COOH); 7.60 – 7.80 (m, 3H, meta to –COOH and ortho to -Cl); 7.52 (dd, 1H, para to –Cl); 7.1 (d, 1H, meta to -Cl); 10.50 (s, 1H, OH).

Preparation of phenol 5

The acid 3 was protected by methyl chloroformate using the procedure described in details previously [1] and transferred into acyl chloride using $SOCl_2$. Then thionyl chloride was evaporated in vacuum and the crude chloride was condensed with 2-methylbutyl lactate 1 in pyridine/dichloromethane solution during 20 hours under reflux. The reaction mixture was poured into water, extracted by dichloromethane, the combined extracts were washed by dilute hydrochloric acid (to remove excess of pyridine) and water and evaporated. The product was stirred in a mixture of tetrahydrofurane and ammonia at room temperature, the reaction was monitored by thin layer chromatography on silica gel. When the reaction was completed the solution was poured into the excess of water and extracted by dichloromethane several times. The organic layer was washed by diluted HCl, twice washed by water, dried by magnesium sulphate and evaporated to dryness.

^{1}H-NMR of 5 ($CDCl_3$, 300 MHz,):

8.12 (d, 2H, ortho to –COO); 7.60 (m, 3H, meta to –COO and ortho to -Cl); 7.42 (dd, 1H, para to –Cl); 7.10 (d, 1H, ortho to -OH); 5.35 (q, 1H, COOC*H); 4.01 (m, 2H, $COOCH_2$), 1.7 (m, 1H, CH_2C^*H), 1.65 (d, 3H, $COOC^*HCH_3$); 1.4 and 1.2 (m, 2H, CH_2CH_3); 0.9 (m, 6H, CH_3).

The synthesis of 4-alkoxybiphenyl-4´-carboxylic acids 6 has been described elsewhere [2]. The final products nZBL were prepared by standard method of esterification with dicyclohexylcarbodiimide in presence of dimethylaminopyridine in dichloromethane. All crude products were purified by column chromatography on silica gel using a mixture

(99.8: 0.2) of dichloromethane and acetone as an eluent and crystallized twice from mixture of ethanol and acetone. Structures of all final products were confirmed by 1H-NMR (300 MHz, Varian). The chemical purity of materials was checked by high pressure liquid chromatography (HPLC), which was carried out with an Ecom HPLC chromatograph using a silica gel column (Separon 7 μm, 3x150, Tessek) with a mixture of 99.8 % of toluene and 0.2 % of methanol as an eluent, and detection of the eluting products by a UV-VIS detector (λ = 290 nm). The chemical purity was found better than 99.8% under these conditions.

^{1}H-NMR of 7ZBL ($CDCl_3$, 300 MHz):

8.30 (d, 2H, ortho to –COOAr); 8.18 (d, 2H, ortho to –COOC*H); 7.60 – 7,80 (m, 8H, ortho to -Ar); 7.40 (d, 1H, meta to –Cl); 7.00 (d, 2H, ortho to -OCH_2); 5.38 (q, 1H, COOC*H); 4.00 (m, 4H, CH_2OAr and $COOCH_2$), 1.67 (d, 3H, CH_3CH*COO), 1.7 and 1.3 (m,13H, CH_2, CH); 0.9 (m, 9H, CH_3).

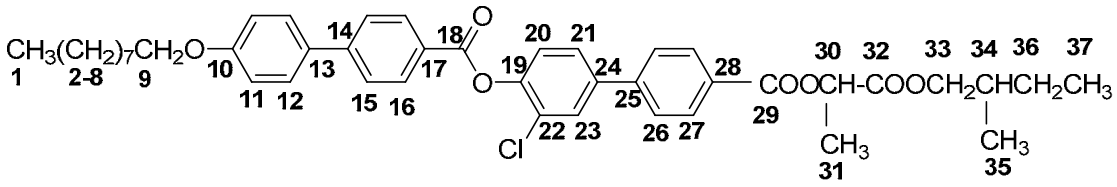
^{1}H-NMR of 9ZBL ($CDCl_3$, 300 MHz):

8.30 (d, 2H, ortho to –COOAr); 8.19 (d, 2H, ortho to –COOC*H); 7.60 – 7,80 (m, 8H, ortho to -Ar); 7.42 (d, 1H, meta to –Cl); 7.00 (d, 2H, ortho to -OCH_2); 5.39 (q, 1H, COOC*H); 4.00 (m, 4H, CH_2OAr and $COOCH_2$), 1.69 (d, 3H, CH_3CH*COO), 1.7 and 1.3 (m,17H, CH_2, CH); 0.9 (m, 9H, CH_3).

^{1}H-NMR of 10ZBL ($CDCl_3$, 300 MHz):

8.30 (d, 2H, ortho to –COOAr); 8.20 (d, 2H, ortho to –COOC*H); 7.60 – 7,80 (m, 8H, ortho to -Ar); 7.40 (d, 1H, meta to –Cl); 7.02 (d, 2H, ortho to -OCH_2); 5.38 (q, 1H, COOC*H); 4.00 (m, 4H, CH_2OAr and $COOCH_2$), 1.70 (d, 3H, CH_3CH*COO), 1.7 and 1.3 (m,19H, CH_2, CH); 0.9 (m, 9H, CH_3).

^{13}C-NMR of 9 ZBL ($CDCl_3$, 300 MHz)

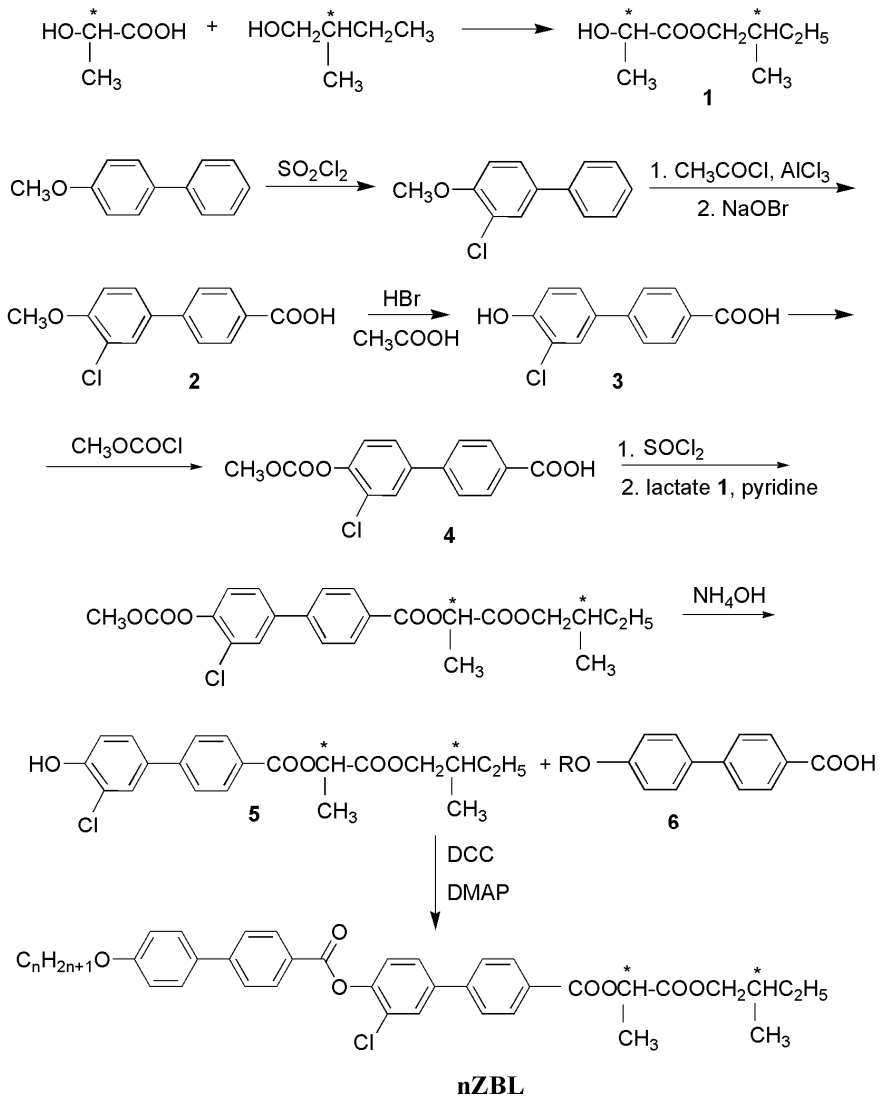


Carbon No.	**Shift (ppm)**	**Carbon No.**	**Shift (ppm)**
1	14.25	23	126.79
9	68.31	24	144.00
10	159.82	25	139.30
11	115.17	26	127.21
12	128.56	27	130.66
13	146.54	28	129.06
14	131.99	29	165.76
15	126.83	30	69.46
16	131.12	31	17.31
17	127.81	32	171.00
18	164.34	33	70.05
19	147.40	34	34.26
20	124.47	35	16.48
21	129.23	36	26.17
22	126.75	37	11.34

Table 1

For **9 ZBL** results taken from ^{13}C-NMR spectroscopy**.**

The molecular structure of all synthesized compounds was checked using standard analytical methods. ^{1}H NMR spectra were acquired on spectrometer Varian-Gemini 300 HC, deuterochloroform, DMSO-d6 serving as solvent and the signals of the solvent were used as internal standards. Chemical shifts are given in the δ-scale (ppm), coupling constant J(H,H) in Hz. IR spectra were recorded on Nicolet FTIR 740 spectrometer in chloroform. Column chromatography was carried out at atmospheric pressure using silica gel (100-200 mesh, Merck).



Scheme ESI

Synthesis route for nZBL compounds preparation.

Texture observation

Planar textures have been observed under polarizing microscope. In Fig 1 and 2 microphotographs are presented.

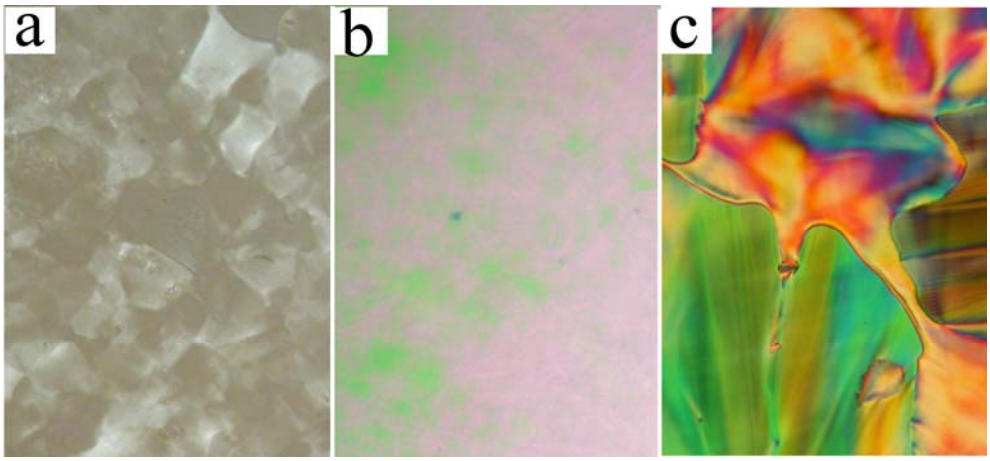


Figure 1 ESI

Planar texture taken in the a) BP at T=174ºC, b) cholesteric phase T=170ºC and c) at the TGBA-SmA* phase transition T=158ºC.

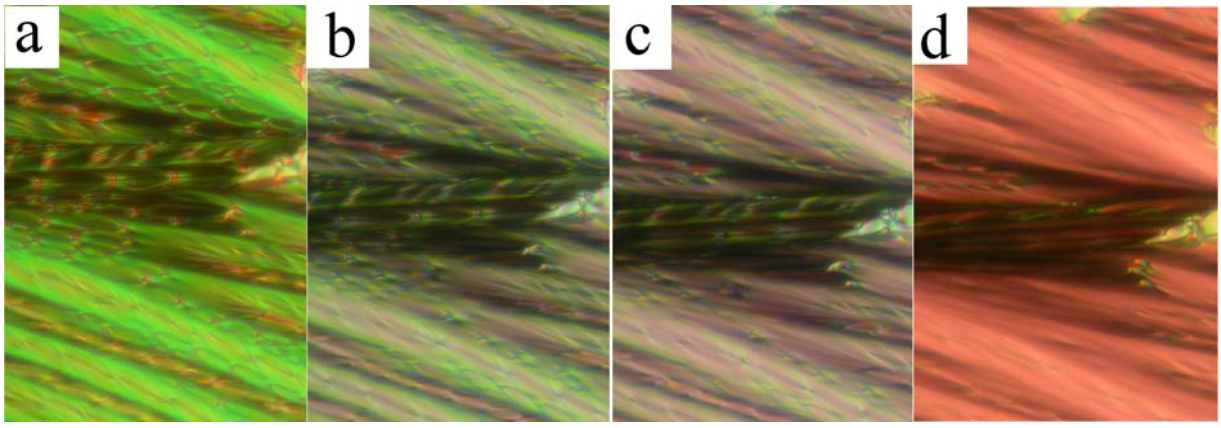


Figure 2 ESI

Fan-shaped texture taken in the a) SmA* at T=130ºC, b) SmA* at T=100ºC, c) SmC* at T=90ºC d) SmA^*_{RE} at T=55ºC.

References

[1] E. Chin, J. W. Goodby, Mol. Cryst. Liq. Cryst., 1986, 141, 311-320.

[2] M. Kaspar, V. Hamplová, V. Novotná, M. Glogarová D. Pociecha., P. Vanek, Liquid Crystals, 2001, 28 (8), 1203-1211.