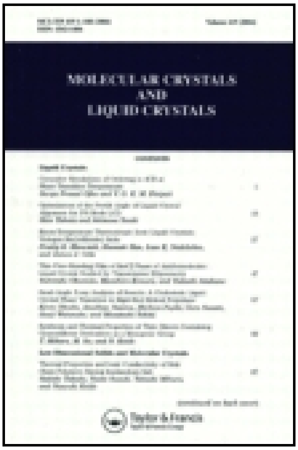

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystalline Properties of S-(-)-4-(2-n-Alkoxy-Propionyloxy) Biphenyl-4′-n-Alkoxy-3,5-Dimethylbenzoate

Anikó Vajda [a] , Miroslav Kašpar [b] , Věra Hamplová [b] , Přemysl Vaněk [b] , Katalin Fodor-csorba [a] & Lajos Bata [a]

[a] Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, H-1525, Budapest, P.O.Box 49, Hungary

[b] Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221, Prague, 8, Czech Republic

Version of record first published: 24 Sep 2006

To cite this article: Anikó Vajda, Miroslav Kašpar, Věra Hamplová, Přemysl Vaněk, Katalin Fodor-csorba & Lajos Bata (2000): Liquid Crystalline Properties of S-(-)-4-(2-n-Alkoxy-Propionyloxy) Biphenyl-4′-n-Alkoxy-3,5-Dimethylbenzoate, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 351:1, 279-286

To link to this article: http://dx.doi.org/10.1080/10587250008023277

Mol. Cryst. and Liq. Cryst., 2000, Vol. 351, pp. 279-286
Reprints available directly from the publisher
Photocopying permitted by license only

Liquid Crystalline Properties of S-(-)-4-(2-n-Alkoxy-Propionyloxy) Biphenyl-4′-n-Alkoxy-3,5-Dimethylbenzoate

ANIKÓ VAJDA[a], MIROSLAV KAŠPAR[b], VĚRA HAMPLOVÁ[b],
PŘEMYSL VANĚK[b], KATALIN FODOR-CSORBA[a] and LAJOS BATA[a]

[a]*Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, H-1525 Budapest, P.O.Box 49, Hungary and* [b]*Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221 Prague 8, Czech Republic*

Four new chiral homologous series of ferroelectric liquid crystals S-(-)-4-(2-n-alkoxy-propionyloxy)biphenyl-4′-n-alkoxy-3,5-dimethylbenzoate (**DMn/*m*** series) having O-substituted S-(-)-lactic acid as terminal group were synthesized, and characterized. They showed monotropic chiral smectic C and chiral nematic mesophases, and two representatives exhibited blue phase as well. Binary mixtures of these compounds were investigated. The effect of the lateral methyl substitutents and the length of the terminal groups on the chiral and non-chiral parts were investigated.

Keywords: ferroelectric liquid crystals; synthesis; lactic acid derivatives

INTRODUCTION

The synthesis of S-(-)-4-(2-n-alkoxy-propionyloxy)biphenyl-4'-n-alkoxy-benzoate (**H*n/m***) series was described earlier[1]. These materials containing S-(-)-2-alkoxypropionate chiral unit exhibited in a wide temperature range of ferroelectric phase with high value of spontaneous polarization (P_s). We have reported recently another series

(**M*n/m***)[2], having the same chiral unit but containing lateral methyl substituent in ortho position to the alkoxy chain of the alkoxybenzoic unit. In comparison with the **H*n/m*** series[1] the SmC* range of this **M*n/m*** series was shifted to room temperature. These methyl substituted analogues showed also high P_s[2].

Our present work is a continuation of the studies on **M*n/m*** series, but we used the 3,5-dimethyl substituted alkoxy benzoic acid derivatives. The mesomorphic behaviour of the homologous series of (S)-(-)-4-(2-n-alkoxy-propionyloxy)biphenyl-4'-n-alkoxy-3,5-di-methyl-benzoates (**DM*n/m***) and their binary mixtures was investigated.

SYNTHESIS

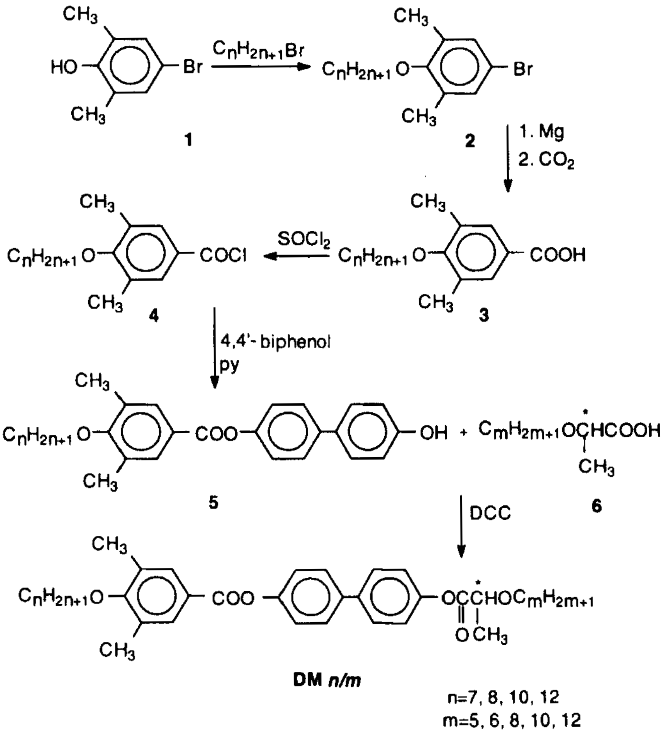

FIGURE.1 Synthesis of **DM*n/ m*** series

The general procedure for the preparation of the **DM*n*/*m*** series is summarized in Fig.1. The intermediates and final products were characterized by ^{1}H-NMR spectroscopy (200 MHz) in $CDCl_3$ using a Varian NMR spectrometer at 25°C, band assigments were carried out by a two dimensional (COSY) method.

4-bromo-2,6-dimethyl-alkoxybenzene (2): 4-bromo-2,6-dimethyl-phenol (**1**) (0,3 mol) was dissolved and reacted in dioxane (400 ml) with an appropriate alkylbromide (0,3 mol) in the presence of KOH (0,5 mol). The reaction mixture was heated under reflux for 4 days, then the resulting solution was poured into one liter of water, extracted with ether, washed twice with water, dried over KOH and distilled in vacuum (yield 82-90%) for n=7 bp.:190°C/8Hgmm.

3,5-dimethyl-4-alkoxybenzoic acids (3): The solution of **2** in 5 ml of 1,2-dichloroethane was added dropwise to a mixture of 1 mol of magnesium turnings and 400 ml of dried tetrahydrofurane. After the addition was complete, the mixture was heated under reflux for 5 hours. The cold mixture was poured into 500 g of CO_2 and stored in the refrigerator over night. Diluted HCl was then added to the solid yellow residue, the product was extracted with ether and the organic layer evaporated to dryness. The light yellow crystals of **3** (54 % yield) were used after recrystallization from ethanol, Mp.: **n**=8: 79°C. ^{1}H NMR (200 MHz, $CDCl_3$): **n**=8: 7,80 (2H,s,HAr); 3,80 (2H,t,OCH_2); 2,32 (6H,s,CH_3Ar); 1,8 (2H,quint,$OCH_2\underline{CH_2}$); 1,5 (2H,quint,$OCH_2CH_2\underline{CH_2}$); 1,3 (8H,m,$CH_2$); 0,90 (3H,t,$CH_3$).

4-n-alkoxy-3,5-dimethyl-benzoyl chloride (4): obtained after thionyl-chlorid transformation of **3**.

(4-hydroxy-biphenyl)-4-n-alkoxy-3,5-dimethylbenzoates (5): The mesogenic phenols (**5**) were prepared from 3,5-dimethyl-4-alkoxy-benzoyl chlorides by reaction with 4,4'-dihydroxybiphenyl in pyridine/dichloromethane solution. The products were crystallized from ethanol. Mp. (%). ^{1}H NMR for **n**=8: 7,90 (2H, s, ArH ortho to CH_3); 7,54 (2H,d,ArH meta to OCO); 7,41 (2H,d,ArH meta to OH); 7,22 (2H,d,ArH ortho to OCO); 6,84 (2H,d,ArH ortho to OH); 3,83 (2H, t,ArOCH_2); 2,36 (6H,s,CH_3Ar); 1,82 (2H,quint,$OCH_2\underline{CH_2}$); 1,2-1,6 (10H,m,CH_2); 0,90 (3H,t,CH_3).

The **(S)-(-)-2-alkoxypropionic acids (6)** were obtained by alkylation of (S)-(-)-ethyl-lactate with appropriate alkyliodide in the presence of Ag_2O [1].

(S)-[4-(2-alkoxy-propionyloxy)-biphenyl]-4-n-alkoxy-3,5-dimethyl-benzoates (DMn/*m*) were obtained by esterification using dicyclohexylcarbodiimid (DCC) as condensation agent in solvent at room temperature using p-dimethylaminopyridine as catalyst. The crude products were chromatographed on silica gel (Kieselgel 60, Merck, Darmstadt) in a mixture of 1% ethanol, 99% CH_2Cl_2 and crystallized from methanol. The product purity was determined by analytical high pressure liquid chromatography using a silica gel column (Biospher SI 100, 250x4, Watrex) eluted with a mixture of 99.9% toluene and 0,1 % methanol and detecting the products by UV-VIS detector (λ=290 nm). For all compounds the optical rotation was measured, the specific rotations were nearly the same, ranging from $[\alpha]_D^{25}$=-32.0 (c=0.1; $CHCl_3$) for **DM7/6** to $[\alpha]_D^{25}$=-31.0 (c=0.1; $CHCl_3$) for **DM12/12**. ^1H NMR **DM8/10**: 7,90 (2H,s,ArH ortho to CH_3); 7,6 (4H,dd, ortho to Ar-Ar); 7,26 (2H,d,ArH ortho to ArCOO-); 7,19 (2H,d,ArH ortho to *CHCOO); 4,2 (1H,q,*C$\underline{H}$-CH_3); 3,83 (2H,t, ArO$\underline{CH_2}$); 3,7 and 3,5 (1H,1H,m,$\underline{CH_2}$OCH*); 2,36 (6H,s,$\underline{CH_3}$Ar); 1,82 (2H,quint, ArOCH_2 - $\underline{CH_2}$); 1,60 (3H,d,$\underline{CH_3}$CH*); 1,7-1,2 (26H,m,CH_2); 0,9 (6H,m,CH_3).

TEXTURE INVESTIGATIONS

The textures of liquid crystals and their mixtures were observed in thin film form between glass slides using an Amplival Pol-U polarizing microscope equipped with a Boetius heating-stage. The heating rate was 4°C/min, the cooling rate was not controlled. Differential Scanning Calorimetry (DSC) measurements were carried out by a Perkin Elmer DSC7 equipment, using 5K/min heating and cooling rate in nitrogen atmosphere.

The data observed by polarizing microscopy were in good accordance with that of the DSC measurements (Table 1). If the DSC data were available, in these cases the additional values are given in Table 1 by bold letters.

Phase diagrams of four homologous series were investigated (Fig.2a-d). The melting points of the compounds are between 51°C (**DM10/6**, Fig.2c) and 78°C (**DM8/5**) (Fig.2b). The melting behaviour of **DM7/5** - **DM7/12** (Fig2a) show the classic odd-even effect with increasing terminal chain length. The chiral nematic phase (N*) appeared at the shorter alkoxy chains **DM*n*/5-10** on the chiral side

DM n/m	**m.p. T(°C) /ΔH(J/g)**	**I**	**T(°C) /ΔH (J/g)**	**N***	**T(°C) /ΔH (J/g)**	**SmC***	**T(°C) /ΔH (J/g)**	**Cr**
7/5	68.3 / 83.7	•	54.1 /-0.9	•	32.6 / -2.9	•α	**32**	•
7/6	59.9 / 75.3	•	52.6 /-0.8	•	35.8 / -2.9	•	**30**	•
7/10	73.0 / 100.2	•	**43.5** δ	• β	**40**	• β	46.7 / -61.0 **30**	•
7/12	75.9 / 92.1	•	-	-	-	-	52.8 / -89.1	•
8/5	78.3 / 89.8 β	•	58.8 /-1.0	•	-	-	44.1 / -58.4	•
8/6	67.0 / 83.4 β	•	57.4 /-1.0	•	41.1 / -2.3 **44**	•	39.8 / -57.8	•
8/10	63.2 / 82.4	•	47.7 / <0.15 ε	•	46.2 / -2.0	•	42.6 / -57.5	•
8/12	69.8 / 78.3	•	**51**	•	-	-	56.8 / -77.0	•
10/6	55.2 / 85.5	•	56.3 /-1.1	•	43.6 / -1.7	•	39.9 / -41.4	•
10/8	62.3 / 99.2	•	53.1 /-1.6	•	49.1 / -3.5	•	**38**	•
10/10	74.0 / 94.3	•	51.6	•	**50**	•	49.5 / -75.7	•
10/12	70.3 / 87.0	•	-	-	**51.5**	β	55.7 / -80.9	•
12/5	64.8 / 84.2	•	54.4 / -1.2	•	-	-	51.7 / -51.4	•
12/6	62.8 / 90.1	•	53.3 / -1.5	•	-	-	49.3 / -78.1	•
12/8	62.6 / 91.5	•	53.7 /-2.3	•	52.1 / -3.1	•	43.8 / -76.3	•
12/10	71.9 / 91.9	•	-	-	56.0 / -5.2	•	41.0 / -46.8	•
12/12	73.9 / 98.9	•	-	-	57.0 /24.6γ **63**	•γ	42.8 / -47.3	•

Symbols: • the phase exists; - the phase does not exist. α: The transition to SmC* phase was observed by DSC, no crystallization was observed till 20°C, β: Phase not observed by DSC, γ: The transition entalphy of crystallization is superimposed with that of the SmC* phase. δ: Bph **50**°C, ε: Bph **54**°C.

TABLE 1 Phase transition temperatures for **DM*n/m*** series obtained by DSC measurements and optical microscopy (bold values).

except compound **DM*12/10*** and at the longer chain lenghts, only at **DM*8/12***. Almost all the members of these series have a N* phase which was identified from the focal conic or Grandjean plane textures. The blue phase (Bph) appeared at two compounds **DM*7/10*** and **DM*8/10*** bearing short non-chiral alkoxy chain. Almost every member of the homologous series exhibited chiral smectic phase (SmC*) except the members with shorter alkoxy chiral chain like **DM*8/5***, **DM*12/5*** and **DM*12/6***. This ferroelectric phase was identified from broken fan-shaped or schlieren textures in thin samples. It can be seen in the phase diagrams (Fig.2a) for **DM*7/5*-DM*7/10*** and **DM*10/8*** (Fig.2c) these ferroelectric phases can be supercooled well below the melting points. Only one compound **DM*7/12*** has a vey short supercoolable range, but has no mesophase.

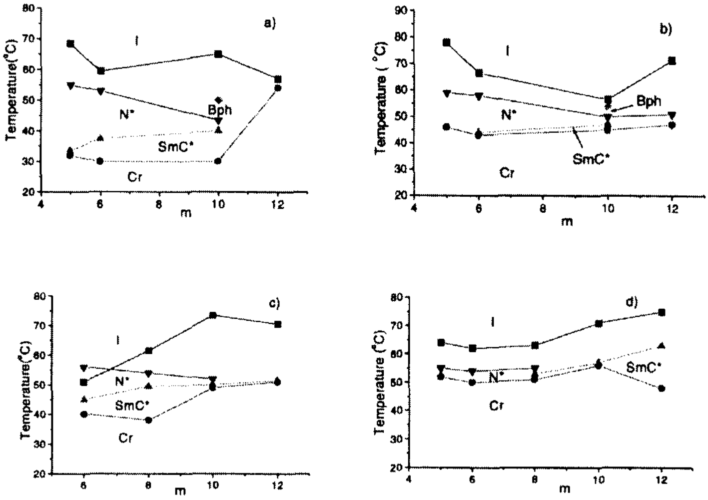

FIGURE 2a-d: Phase diagrams of the homologous series a) **DM*7/m***, b) **DM *8/m***, c) **DM*10/m***, d) **DM*12/m***. Melting p are denoted by squares, I-N phase transitions by "down" triangles, N-SmC* and I-SmC* phase transitions by "up" triangles, recrystallization temperatures by circles.

BINARY MIXTURES

Inspired by our previous works[3,4] binary mixtures (**BM**) were prepared. In order to study the effect of terminal and lateral substituents on the SmC* phase, miscibility studies were carried out (Table 2).

The strategy was to mix compounds with different cores like 3-methylbenzoate derivative **M*8/10*** with the 3,5-dimethyl substituted analogues as **DM*8/10*** (**BM8**) while keeping the terminal substituents constant. In this mixture the SmC* phase temperature range has been broadened, but remained monotropic, only the N* phase became enantiotropic. If the components of the mixture had the length of **n/m** groups in opposite sense, like in **BM7** mixture, then the N* phase disappeared and the SmC* phase remained monotropic.

We have changed the chain length of the chiral part, keeping constant both the core and the non-chiral chain length. The mixtures of **BM1-BM6** were composed of members of the **DM*n/m*** series with chiral chains differing from each other by four carbon atoms in length. These mixtures exhibited enantiotropic SmC* phase. Presumably the intercalated tail-to-tail packing of the molecules stabilizes the ferroelectric phase, making it enantiotropic. It should be mentioned, that though both the individual components of **BM1** showed N* phase, and one of them Bph as well, the N* phase disappeared in their binary mixture at eutectic concentration. It might indicate a close packing of the constituent molecules which align themselves in a smectic layer structure.

Mix.	Comp.	Wt %	m.p.	Cr	SmC*	N*	I
BM1	**DM7/6** **DM7/10**	50 50	46.5	•(30)	•51	-	•
BM2	**DM10/8** **DM10/12**	60 40	45	•(38)	•48	•53.5	•
BM3	**DM10/8** **DM10/12**	46.7 53.3	45	•(37)	•49	•53	•
BM4	**DM12/8** **DM12/12**	44.1 45.9	50	•(37)	•54	•55	•
BM5	**DM12/8** **DM12/12**	43.2 56.8	52	•(40)	•54	-	•
BM6	**DM12/8** **DM12/12**	40 60	54	•(40)	•55	-	•
BM7	**DM10/8** **M8/10**	33.3 66.7	78	•(55)	•(72)	-	•
BM8	**DM8/10** **M8/10**	50 50	57	•(40)	•(55.5)	•59	•
BM9	**DM7/5** **DM12/12**	60 40	51	•(28)	•(36)	•51	•
BM10	**DM7/5** **DM12/12**	40 60	52	•(40)	•(42)	•52	•
	M8/10	100	76	•(34)	•76	-	•

( ): monotropic phase; temperatures in °C

TABLE 2 Phase behaviour of binary mixtures

If the difference of the terminal chains is larger than four carbon atoms of the components (**BM9, BM10**) the SmC* phase remains monotropic in the mixtures.

CONCLUSION

The individual members of **DM*n/m*** series have monotropic SmC* phase. The binary mixtures (**BM1-BM6**) prepared from the members of this series differ from each other by four carbon atoms on the chiral part (**m**) and having the same alkoxy chain length (**n**) on the non-chiral part, show enantiotropic SmC* and in some cases N* phase as well. Presumably the intercalated tail-to-tail packing of the molecules stabilizes the ferroelectric phase, making it enantiotropic. This stabilizing effect is not observed in the mixtures prepared from compounds with different cores (e.g members of **M*n/m*** and **DM*n/m***) with the same terminal chains both on the chiral and the non-chiral parts (**BM8**). If the components of the mixtures have the same core and differ from each other by more than four carbon atoms on both terminal chains (**BM9, BM10**), show only monotropic ferroelectric phase. Probably the intercalated tail-to-tail packing of the molecules can not develop.

The packing of the molecules in the mixtures are under investigation by X-ray.

ACKNOWLEDGEMENT

This work was supported by the Hungarian Research Fund OTKA T020905, T030401 and by the Grant Agency of the Czech Republic, Grant No.202/99/1120. The authors are thankful to professor W. Weissflog and Dr. Nándor Éber for helpful discussions, and to Éva Sásdi and Margit Molnár for the technical assitance.

References

[1] M. Kašpar, M. Glogarová, V. Hamplová, H. Sverenyák, S.A. Pakhomov, *Ferroelectrics*, **148**. 103 (1993).

[2] M. Kašpar, V. Hamplová, S. A. Pakhomov, I. Stibor, H. Sverenyák, A. Bubnov, M. Glogarová, P.Vanek, *Liquid Crystals*, **22**. 557 (1997).

[3] A. Vajda, K. Fodor-Csorba, L. Bata, T. Paksi, Zs. Kakas, I. Jánossy, J. Hajtó, *Mol. Cryst. Liq. Cryst.*, **289**. 89 (1996).

[4] K. Fodor-Csorba, E. Szabó, A. Vajda, L. Bata, G. Galli, S. Holly, E. Gács-Baitz, K. Újszászy, L.C. Chien, *Liquid Crystals*, **24**. 861 (1998).