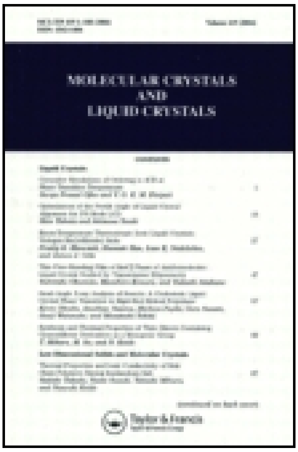


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of New Liquid Crystals with 2,3,4,9-Tetrahydro-1H-Fluorene Moiety

R. Ch. Geivandov [a] , V. Mezhnev [a] & T. Geivandova [a]
[a] Moscow Fine Organic Synthesis & Liquid Crystal Laboratory "INCORFIN" Ltd. Co, Moscow, Russia

Version of record first published: 14 Jun 2011

To cite this article: R. Ch. Geivandov, V. Mezhnev & T. Geivandova (2011): Synthesis of New Liquid Crystals with 2,3,4,9-Tetrahydro-1H-Fluorene Moiety, Molecular Crystals and Liquid Crystals, 542:1, 141/[663]-148/[670]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.570542

Mol. Cryst. Liq. Cryst., Vol. 542: pp. 141/[663]–148/[670], 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.570542

Taylor & Francis
Taylor & Francis Group

Synthesis of New Liquid Crystals with 2,3,4,9-Tetrahydro-1*H*-Fluorene Moiety

R. CH. GEIVANDOV, V. MEZHNEV, AND
T. GEIVANDOVA

Moscow Fine Organic Synthesis & Liquid Crystal Laboratory
"INCORFIN" Ltd. Co, Moscow, Russia

*A new range of liquid crystals containing the 2,3,4,9-tetrahydro-1*H*-fluorene system have been prepared and its thermal properties were examined. The mesomorphic properties are compared with those of the fluorene and trans-cyclohexane derivatives. Introduction of 2,3,4,9-tetrahydro-1*H*-fluorene in typical liquid crystal structure leads to decrease of melting point and the clearing point values. The chemical structures and mesogenic properties for the reported novel compounds are discussed.*

Keywords 2,3,4,9-tetrahydro-1*H*-fluorene; cross-coupling reaction; liquid crystals

1. Introduction

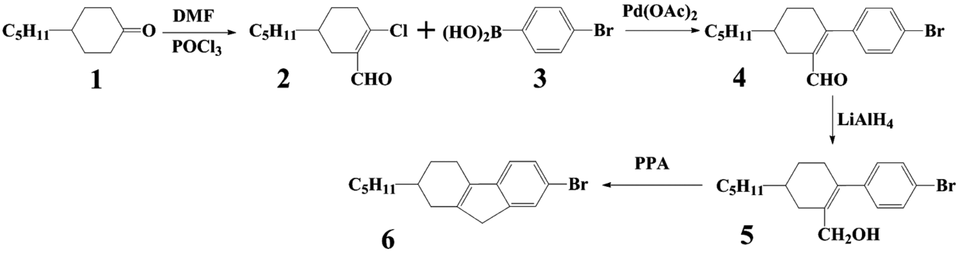
The introduction of alicyclic fragment in the mesogenic moiety of potential liquid-crystalline structure leads to a change in the basic properties of mesomorphic compounds (temperature phase transitions, optical and dielectric anisotropy, viscosity, etc.) [1–4]. In continuation of our systematic studies [5–7] in the area of synthesis of mesomorphic structures, containing mono-, bi- and trialicyclic units, we synthesized a new class of liquid crystals – 2,7-disubstituted 2,3,4,9-tetrahydro-1*H*-fluorene derivatives and investigated their temperature phase transitions.

2. Results and Discussion

2.1. *Synthesis of Target Intermediates and Liquid Crystal*

We thought it was interesting to synthesize an analogue of fluorene, where one of benzene rings is partially hydrogenated. We have concentrated our efforts on the development of convenient synthetic methods for key intermediate products, which provide a new class of liquid crystals – 2,7-disubstituted 2,3,4,9-tetrahydro-1*H*-fluorene derivatives. The syntheses were carried out according to Schemes 1 and 2.

Address correspondence to R. Ch. Geivandov, Moscow Fine Organic Synthesis & Liquid Crystal Laboratory "INCORFIN" Ltd. Co, 27, Burakova str., 111123 Moscow, Russia. Tel.: +7-916-0518677; E-mail: r.ch.geivandov@gmail.com



Scheme 1. Synthesis of 7-Bromo-2-pentyl-2,3,4,9-tetrahydro-1*H*-fluorene (**6**).

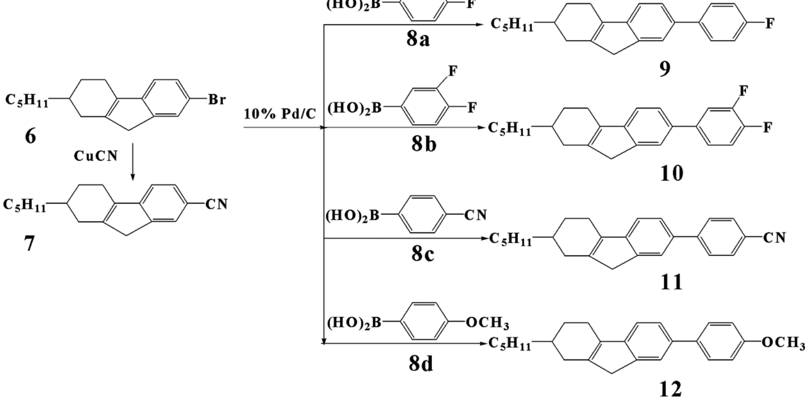
The Scheme 1 in included the following basic subsequent steps:

- obtaining the β-chloracroleine **2** using Vilsmeier-Haack-Arnold method [8] by action of $POCl_3$-DMF complex on ketone **1**,
- cross-coupling of β-chloracroleine **2** with 4-bromophenylboronic acid **3**,
- reduction of aldehyde group in compound **4** using lithium aluminum hydride to obtain alcohol **5**,
- intramolecular dehydration-cyclization of alcohol **5** in the presence of acidic catalysts to obtain compounds **6** with tetrahydrofluorene system.

Although aryl chloride is less reactive due to higher energy barrier for the oxidative insertion of the palladium catalyst into the C-C bond, the Suzuki coupling of vinyl chlorides takes place at a sufficient pace. Moreover, the presence of an electron-accepting group leads to an increase of the reaction rate and allows the use of such derivatives as β-chloracroleine.

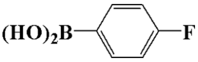
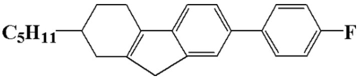
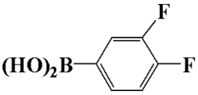
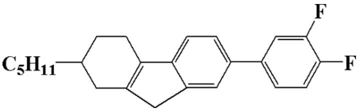
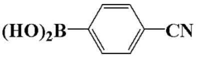
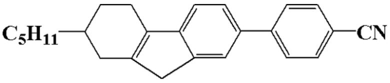
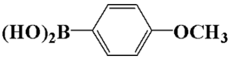
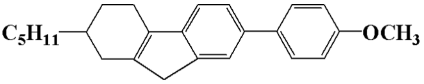
The β-chloracroleine **2** easily went into cross-coupling reaction and the compound **4** was produced in 82% yield.

We have conducted wide investigation while searching for the optimal conditions of cyclization of alcohol **5** by trying various acidic catalysts and reaction conditions variants. The best result for cyclization of alcohol **5** into the compound **6** has been achieved under action of polyphosphoric acid (PPA). The yield of compound **6** was approximately 35%.



Scheme 2. Synthesis of liquid crystals (**9–12**) by cross-coupling reaction.

Table 1. Cross- coupling reaction of 7-bromo-2-pentyl-2,3,4,9-tetrahydro-1*H*-fluorene (**6**) with substituted phenylboronic acids (**8a-d**)

Phenylboronic acids	Product	Yield, %	Ms: m/z (M^+)
		68	334
		77	352
		44	341
		76	346

Compound **6** have been cyanated using cooper cyanide and yielded nitrile **7**. The cross-coupling reaction of compound **6** with 4-substituted phenylboronic acids (**8a-d**) in the presence of 10% Pd/C lead to liquid crystals **9–12** (Scheme 2, Table 1).

2.2. *Liquid Crystalline Properties*

The 2,3,4,9-tetrahydro-1*H*-fluorene is a partially saturated derivative of fluorene. The fluorene moiety differs from a biphenyl unit since it is almost flat and just slightly bent in the plane of the rings. Previous work on fluorene containing mesogens showed them to exhibit mainly smectic phases or very short nematic ranges [9].

Molecule of 2,3,4,9-tetrahydro-1*H*-fluorene (**A**) in contrast to fluorene (**B**) is not flat at all and has a rigid-flexible configuration; both structures are shown on Figure 1.

In this regard, when comparing properties of LC molecules, we also present data on the temperatures for similar trans-cyclohexane derivatives, whose structures combine a rigid-flexible configuration of the core molecule.

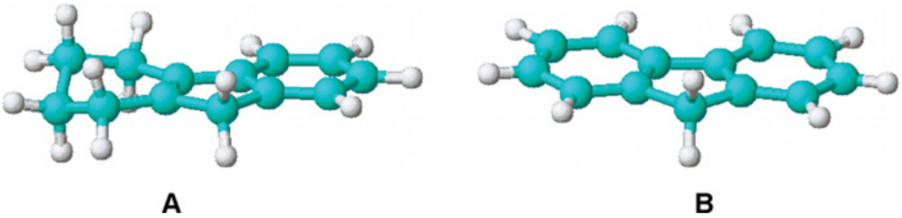


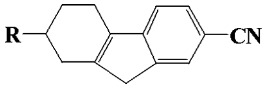
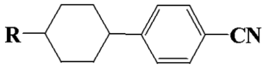
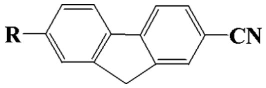
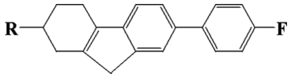
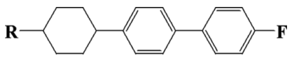
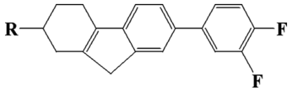
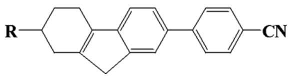
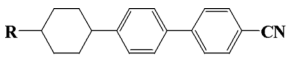
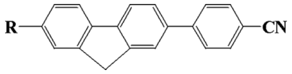
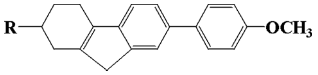
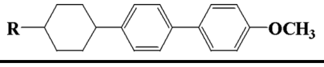
Figure 1. Molecular structures of 2,3,4,9-tetrahydro-1*H*-fluorene (**A**) and fluorene (**B**). (Figure appears in color online.)

As one can see from Table 2, compound **7** and fluorene derivative **7b** with terminal nitrile group exhibit monotropic nematic phase, while compound **7a** has a normal liquid crystalline temperature range.

We have synthesized three units compounds of 2,3,4,9-tetrahydro-1*H*-fluorene (**A**). Compounds **9, 10, 11, 12** (Table 2) have, in contrast to described corresponding trans-cyclohexane derivatives (**9a, 11a, 12a**), lower melting point and give way mainly to thermal stability.

The compounds containing tetrahydro-1*H*-fluorene units **9–12** were found to have nematic and smectic liquid crystalline phase with relatively low phase transition temperature and wide liquid crystalline temperature range.

Table 2. Transition temperatures (°C) for 7-substituted -2-pentyl-2,3,4,9-tetrahydro-1*H*-fluorenes, fluorene and trans-cyclohexane derivatives

Compound	Molecular structure*	Cr	S	N	I	Ref.
7		52	–	·	(34)	–
7A		31	–	·	55	[10]
7B		66	–	·	(24.5)	[9]
9		76	–	·	141	–
9a		100	–	·	152	[11]
10		64	–	·	104	–
11		89	110	·	178	–
11a		96	–	·	222	[12]
11b		128	–	·	216	[13]
12		110	130	·	183	–
12a		80	–	·	165	[14]

*R=C_5H_{11}.

The wide liquid crystalline temperature range of compound **11** and fluorene derivative **11b** are almost comparable, but compound **11** have lower melting and clearing points as compared to compound **11b**.

3. Experimental

All commercially available substances were purchased from Aldrich, Merck, Acros, Fluka or Lancaster and were used without further purification. Solvents were purified and dried if necessary according to standard procedures. All reactions were monitored by thin-layer chromatography on silica gel (Merck, Kieselgel 60, F254). UV-light with wavelength of $\lambda = 254$ nm was used for detection.

3.1. *Melting and Clearing Points*

The temperatures of phase transitions and liquid crystalline phases were observed with Mettler FP 90 coupled with a polarizing Olympus BH-2 microscope. Measured temperatures from the polarizing microscope have been corrected by calibration with standard materials.

3.2. *NMR Spectroscopy*

Confirmations of the intermediate and final product structures were accomplished by ^{1}H, ^{13}C, ^{19}F, NMR spectroscopy (Bruker AM-300 and Bruker Avance II 300 spectrometers) at ambient temperature. Chemical shifts values (δ) are relative to Me_4Si and are given in ppm (references solvents are $CDCl_3$ and DMSO-d6).

3.3. *Mass Spectrometry*

Mass-spectra were obtained directly using Finningan MAT INCOS 50 spectrometer (EI, 70 eV).

*2-Chloro-5-pentylcyclohex-1-ene-1-carbaldehyde (**2**).* To solution of DMF (10.3 ml) in dry chloroform (25 ml) at 5–10 °C was added phosphoryl chloride (10.1 ml) and the mixture was stirred for 10 minutes. Then the 4-pentylcyclohexanone **1** (16.8 ml, 0.1 mol) in chloroform (25 ml) was added drop wise at 20 °C and the mixture was heated at 55–60 °C for 3 hour. The reaction mixture was poured into an aqueous sodium acetate solution (35 g sodium acetate in 120 ml water), extracted with chloroform (3 × 30 ml), and the combined chloroform extracts were washed successively with water and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was distilled to give a colourless liquid.

Yield 82%; bp 92–94 °C at 0.24 mmHg; n_D^{20} 1.4925; ^{1}H NMR($CDCl_3$) δ 0.85 (3H, t, CH_3), 1.2–1.4 (8H, m, C_5H_{11}), 1.45–1.8 (4H, m, cyclohexane), 2.47 (3H, m, cyclohexane), 11,5 (H, s, CHO); ms m/z 214 (M^+).

*2-(4-Bromophenyl)-5-pentylcyclohex-1-ene-1-carbaldehyde (**4**).* A mixture of chloroacroleine **2** (2,59 mmol), 4-bromophenyl boronic acid **(3)** (2,83 mmol), tetrabutylammonium bromide (2,60 mmol), palladium acetate (0,053 mmol, 2 mol %) and potassium carbonate (6,45 mmol) was added to a 10 mL round-bottom flask. Deionized water (5 ml) was added, and the reaction was stirred vigorously for

3 hours at 45 °C. The reaction mixture became dark and non-homogenous. Then the mixture was diluted with water (15 ml), and the product was extracted with EtOAc (3 × 30 ml). The organic phase was stirred over charcoal for 30 min and dried ($MgSO_4$). After filtration and concentration *in vacuo*, the residue was distilled to give a colourless liquid.

Yield is 68%; bp183–190 °C at 0.120 mm Hg; n_D^{20} 1.5660; mp 28–30 °C; ^1H NMR($CDCl_3$) δ 0.9(3H, s, CH_3), 1.2–1.4 (8H, m, C_5H_{11}), 1.45–1.95(4H, m, cyclohexane), 2.5–2.7(3H, m, cyclohexane), 7,1(2H, d, aromatic). 7,5(2H, d, aromatic), 9,48(1H, s, CHO); ms m/z 334 (M^+).

*[2-(4-Bromophenyl)-5-pentylcyclohex-1-en-1-yl]methanol (**5**).* Ether solution (8 ml) of aldehyde **4** (2.1 g, 6.25 mmol) was added to a stirred suspension of lithium aluminum hydride (0.300 g, (7.9 mmol) in dry ether (6 ml) at 0 °C. The temperature was kept at 0 °C for 1 hour. Then reaction mixture was poured into NH_4Cl solution, the product was extracted with ether (3 × 30 mL), combined extracts were washed with water and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/n-hexane). Yield 90%; m.p. 55–56 °C; ^1H NMR ($CDCl_3$) δ 0.9(3H, t, CH_3), 1.2–1.45 (8H, m, C_5H_{11}), 1.75–1.92 (4H, m, cyclohexane), 2.22–2.45 (3H, m, cyclohexane), 3.92 (2H, s, CH_2OH), 7,0(2H, d, aromatic). 7,42(2H, d, aromatic); ^{13}C NMR (DMSO) δ 141.70(C_{arom}-C=C) 135.64(C=C-C_{arom}), 132.86(C_{arom}), 131.92(C_{arom}), 129.93 (C_{arom}), 120.54(C-Br), 63.94(CH_2OH), 36.57(C_{tret}), 32.80, 34.0, 33.7, 32.3, 29.55, 26.69, 22.75(CH_2), 14.14(CH_3); ms m/z 337 (M^+).

*7-Bromo-2-pentyl-2,3,4,9-tetrahydro-1*H*-Fluorene (**6**).* A mixture of (1.5 g, 4.7 mmol) compound **5** and polyphosphoric acid (PPA) (50 g) was heated for 20 minutes at 135–137 °C. The reaction mixture was diluted with water and the product was extracted with ether (3 × 50 ml). The combined organic extracts were washed with water and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/n-hexane).

Yield 35%; m.p. 79–80 °C (acetone); ^1H NMR ($CDCl_3$) δ 0.92(3H, t, CH_3), 1.25–1.48 (8H, m, C_5H_{11}), 1.65–1.8(1H, s, cyclohexane), 1.9–2.1(2H, m, cyclohexane), 2.3–2.55 (3H, m, cyclohexane), 3.2 (2H, s, CH_2), 7,0(1H, d, aromatic). 7,38(1H, d, aromatic), 7,5(1H, d, aromatic); ^{13}C-NMR (DMSO) δ 145.06(C_{arom}-C=C) 141.91(C=C-C_{arom}), 135.49(C_{arom}), 129.04 (C_{arom}), 126.61 (C_{arom}), 118.73(C-Br), 117.49(C_{arom}), 40.42(CH_2), 36.41(C_{tret}), 34.44, 32.54, 32.23, 29.03, 26.87, 22.80, 22.00(CH_2), 14.21(CH_3); ms m/z 318 (M^+).

*2-Pentyl -2,3,4,9-tetrahydro-1*H*-Fluorene-7-carbonitrile (**7**).* A mixture of 7-Bromo-2-pentyl-2,3,4,9-tetrahydro-1*H*-fluorene **6** (0.175 g, 0.55 mmol), copper (I) cyanide (0.58 g, 0.32 mmol) and N-methyl-2-pyrrolidone (5.5 ml) was refluxed in a three-neck flask for 5 hours. Toluene (5 ml) was added, the mixture was cooled, and a solution consisting of ferric chloride (0.65 g), conc. hydrochloric acid (0.16 ml) and water (7.5 ml) was added and it was stirred for 30 minutes at 60–70 °C. The resulting two layers were separated and the resulting organic layer was washed with dilute hydrochloric acid, then with dilute aqueous sodium hydroxide, and further with water. After a small amount of solid matter was eliminated by filtration, toluene was distilled off *in vacuo*. The residue was purified by column chromatography (silica gel/n-hexane).

Yield 65%; transitions (°C) Cr 52 N (34) I; ^{1}H NMR ($CDCl_3$) δ 0.92(3H, t, CH_3), 1.25–1.45 (8H, m, C_5H_{11}), 1.65–1.8(1H, s, cyclohexane), 1.9–2.15(2H, m, cyclohexane), 2.3–2.62(3H, m, cyclohexane), 3.3(2H, s, CH_2), 7,0(1H, d, aromatic). 7,22(1H, aromatic), 7,58(1H, aromatic); ms m/z 265 (M^+).

*General procedure for cross- coupling reaction of 7-bromo-2-pentyl-2,3,4,9-tetrahydro-1*H*-fluorene (5) with substituted phenylboronic acids (**8a-d**).* 7-Bromo-2-pentyl-2,3,4,9-tetrahydro-1H-fluorene **6** (4.38 mmol), substituted phenylboronic acid **8a-d** (4.38 mmol), 10% Pd/C (0.01 g), triphenylphosphine (0.18 mmol) and sodium carbonate (8.76 mmol) were heated in a mixture of toluene (1 ml), ethanol (0.5 ml) and water (0.3 ml) for 24 hours at 80 °C. The reaction mixture was diluted with water, the product was extracted with EtOAc and the combined extracts were washed with water, filtered, dried (Na_2SO_4). The solvents were removed *in vacuo* and the residue was purified by column chromatography (silica gel/n-hexane).

*7-(4-Fluorophenyl)-2-pentyl-2,3,4,9-tetrahydro-1*H*-fluorene (**9**).* Yield 68%; transitions (°C) Cr 76 N 141 I; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t), 1.20–2.7 (15H, m), 3.3 (2H, m), 7.05–7.6 (7H, m, arom). ^{19}F-NMR (DMSO): δ 138.5.

*7-(3,4-Difluorophenyl)-2-pentyl-2,3,4,9-tetrahydro-1*H*-fluorene (**10**).* Yield 77%; transitions (°C) Cr 64 N 104 I; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t), 1.20–1.5 (8H, m), 1.75 (1H, s), 1.9–2.2 (2H, m), 2.3–2.65 (3H, m), 3.3 (2H, s, CH_2), 7.1–7.55 (6H, m, arom). ^{19}F NMR ($CDCl_3$): δ 138.5 (d, 1 F), 142.45(d, 1 F).

*4-(2-Pentyl-2,3,4,9-tetrahydro-1*H*-fluoren-7-yl)benzonitrile (**11**).* Yield 44%; transitions (°C) Cr 89 S 110 N 178 I;^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t), 1.25–2.6 (15H, m), 3.3 (2H, m), 7.25–7.7 (7H, m, arom.).

*7-(4-Methoxyphenyl)-2-pentyl-2,3,4,9-tetrahydro-1*H*-fluorene (**12**).* Yield 76%; transitions (°C) Cr 110 S 130 N 183 I; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t), 1.25–2.6 (15H, m), 3.29 (2H, m), 3.85 (3H, s, OCH_3), 7.0–7.6 (7H, m, arom.).

4. Conclusions and Perspectives

For the first time a new class of nematic liquid crystal compounds containing 2,3,4,9-tetrahydro-1*H*-fluorene system has been synthesized and characterized.

We can conclude that the replacement of rigid fragments in the typical LC molecules with rigid-flexible fragments changes the whole set of their properties. Molecular factors can be divided into three groups – geometry, dispersion, and polarity. They all have an impact on the mesomorphic behavior of molecules.

The relative importance of each factor depends on the characteristics of chemical, electronic and spatial structure of the molecule. In this regard, sequential

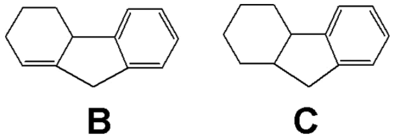


Figure 2. Structures of 2,3,4,4a,9-tetrahydro-2H-fluorene (**C**) and trans-2,3,4,4a,9,9a-hexahydro-1*H*-fluorene (**D**) mesogenic moiety.

analysis of each of these factors on the example of the LC classes allows us to estimate the contribution of factor in the total effect of changes in respect of thermal stability and mesophase range.

In future, we plan to synthesize new LC structures, containing 2,3,4,4a,9-tetrahydro-2H-fluorene (**C**) and trans-2,3,4,4a,9,9a-hexahydro-1*H*-fluorene (**D**) systems (Figure 2).

References

[1] Eidenschink, R., Haas, O., Romer, M., & Scheuble, B. S. (1984). *Angew. Chem.*, *96*, 151.

[2] Eidenschink, R., & Scheuble, B. S. (1986). *Mol. Cryst. Liq. Cryst. Lett.*, *3*, 33.

[3] Gray, G. W., & Kelly, S. M. (1981). *Mol. Cryst. Liq. Cryst.*, *75*, 95.

[4] Petrov, V. F., Torgova, S. I., Karamysheva, L. A., & Takenaka, S. (1999). *Liquid Crystals*, *26*, 1141.

[5] Geivandov, R. Ch., Goncharova, I. V., & Titov, V. (1989). *Mol. Cryst. Liq. Cryst.*, *166*, 101.

[6] Karamysheva, L. A., Geivandova, T. A., Agafonova, I. F., Roitman, K. V., Torgova, S. I., Geivandov, R. Ch., Petrov, V. F., & Grebyonkin, M. F. (1990). *Mol. Cryst. Liq. Cryst.*, *191*, 237.

[7] Barnik, M. I., Geivandov, R. Ch., Gorina, I. I., & Shtykov, N. M. (1998). *Mol. Mat.*, *2*, 1.

[8] Arnold, Z., & Zemlicka, J. (1959). *Collect. Czech. Chem. Commun.*, *24*, 2385.

[9] Davison, I. R., Hall, D. M., & Sage, I. (1985). *Mol. Cryst. Liq. Cryst.*, *129*, 17.

[10] Eidenschink, R., Erdmann, D., Krause, J., & Pohl, L. (1977). *Angew. Chem.*, *89*, 103.

[11] Eidenschink, R. (1983). *Mol. Cryst. liq. Cryst.*, *94*, 119.

[12] Eidenschink, R., Erdmann, D., Krause, J., & Pohl, L. (1977). *Angew. Chem. Int. Ed. Engl.*, *16*, 100.

[13] Boardman, F. H., Dunmur, D. A., Grossel, M. C., & Luckhurst, G. R. (2002). *Chem. Lett.*, *31*, 60.

[14] Demus, D., Goodby, J. W., Gray, G. W., Spiess, H.-W., & Vill, V. (1997). *Handbook of Liquid Crystals*, Wiley: New York.