Molecular Crystals and Liquid Crystals

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

New Liquid Crystalline 3,5-disubstituted 4,5-dihydro-1,2-oxazoles

V. Bezborodov [a] , N. Kauhanka [a] & V. Lapanik [a]

[a] Institute of Applied Physics Problems, Minsk, Belarus

Version of record first published: 18 Oct 2010

To cite this article: V. Bezborodov, N. Kauhanka & V. Lapanik (2004): New Liquid Crystalline 3,5-disubstituted 4,5-dihydro-1,2-oxazoles, Molecular Crystals and Liquid Crystals, 411:1, 103-110

To link to this article: http://dx.doi.org/10.1080/15421400490434874

Mol. Cryst. Liq. Cryst., Vol. 411, pp. 103/[1145]–110/[1152], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490434874

NEW LIQUID CRYSTALLINE 3,5-DISUBSTITUTED 4,5-DIHYDRO-1,2-OXAZOLES

V. Bezborodov, N. Kauhanka, and V. Lapanik
Institute of Applied Physics Problems, Minsk 220064, Belarus

The synthesis and mesomorphic properties of new liquid crystalline 3,5-disubstituted 4,5-dihydro-1,2-oxazoles (Δ^2-isoxazolines) are discussed. These derivatives of isoxazoline have been synthesized by the interaction of the corresponding oximes and unsaturated compounds in the presence of N-chlorosuccinimide and triethylamine

Keywords: 3,5-disubstituted 4,5-dihydro-1,2-oxazoles (Δ^2-isoxazo-lines); synthesis of liquid crystals

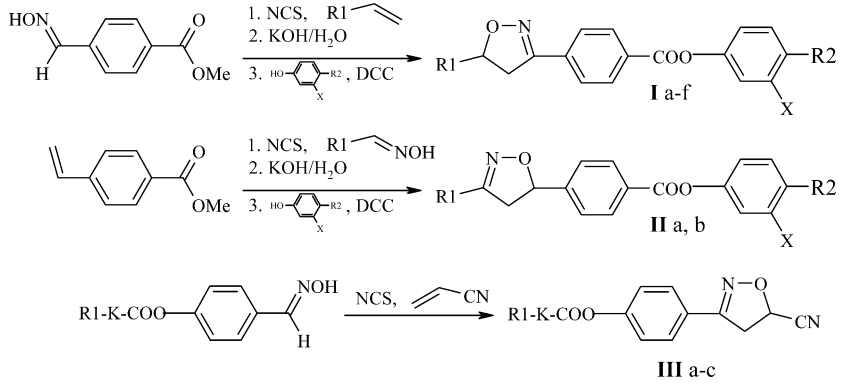
INTRODUCTION

There have been many reports of liquid crystalline compounds containing five-membered heterocyclic rings [1–4]. It was found that non-linear heterocyclic liquid crystals, such as pyrazole, thiophene, furane and isoxazole derivatives with a terminally-positioned heterocyclic ring form smectic or nematic phase at low temperature and in wide temperature range. In addition, the presence of hetero-atoms leads to the increasing of the molecular dipole and the dielectric anisotropy. These parameters are very important in the design of new compounds, which are in turn useful components for liquid crystalline mixtures for display application. In a previous publication we described the properties of liquid crystals containing isoxazole or isoxazoline fragments as a central bridge in the mesogenic core [5]. In continuation of these investigations we synthesized novel chiral and non-chiral liquid crystalline aryl esters of 4-(5-alkyl-4,5-dihydro-1,2-oxazol-3-yl)benzoic (**I**), 4-(3-alkyl-4,5-dihydro-1,2-oxazol-5-yl)benzoic (**II**) acids and 4-(5-cyano-4, 5-dihydro-1,2-oxazol-3-yl)phenyl esters of 4-alkoxybenzoic acids (**III**) and investigated their mesomorphic properties with a particular interest in their structure-property relationships.

Address correspondence to V. Bezborodov, Institute of Applied Physics Problems, Minsk 220064, Belarus.

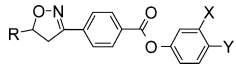
The esters (**I** and **II**) were prepared in yield 70–80% using 1,3-dipolar cycloaddition of corresponding nitrile oxides to 1alkenes or methyl ester of 4-styrylbenzoic acids and than the following base hydrolysis of the methyl esters and the esterification of prepared acids with various phenols in the presence of dicyclohexylcarbodiimide (DCC) and 4-N,N-dimethylaminopyridine as catalyst. The cyano-derivatives (**III**) we synthesized using the same interaction of oximes of 4-(4-alkoxybenzoyloxy)benzaldehydes or 4-(*trans*-4-pentylcyclohexanoyloxy)benzaldehyde with acrylonitrile in the presence of N-chlorosuccinimide and triethylamine (see Scheme).

The phase transition temperatures of 3,5-disubstituted 4,5-dihydro-1,2-oxazoles (**I–III**) are listed in the Tables 1–3. As can be seen from the tables, aryl esters of 4-(5-alkyl-4,5-dihydro-1,2-oxazol-3-yl)benzoic (**I a–f**) are characterized by the formation of the nematic or smectic A or B phases in temperature range 85–154°C. It should be noted that ethyl and chiral carboxyalkyl derivatives (**I a,b,e,f**) form smectic phases, whereas only the nematic phase is observed for the corresponding fluorocyano derivatives (**I c,d**). The rearrangement of the substituents in the heterocyclic fragment leads to the disappearance of the mesomorphic properties and the melting point depression for the aryl esters of 4-(3-alkyl-4,5-dihydro-1,2-oxazol-5-yl)benzoic acids (**II a,b**) (see Table 2). It can be explained by a weakening of the intermolecular interactions from 3-aryl-5-alkyl to 3-alkyl-5-aryl derivatives in the result of the narrowing of the electronic conjugation and the disruption the overall symmetry of the molecule. 4-(5-Cyano-4,5-dihydro-1,2-oxazol-3-yl)phenyl esters of 4-alkoxybenzoic and *trans*-4-pentylcyclohexane carboxylic acids (**III a–c**) (see Table 3)

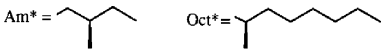


SCHEME R1 = $H_{17}C_8O$-$H_{21}C_{10}O$; H_9C_4, $H_{11}C_5$; K = benzene or cyclohexane ring; X = H or F; R2 = CN, C_2H_5, $COOCH_2CH(CH_3)C_2H_5$, $COOCH(CH_3)C_6H_{13}$, $C_6H_4COOCH(CH_3)C_6H_{13}$.

TABLE 1 Yields, Transition Temperatures of 3-aryl-5-alkyl 4,5-dihydro-1,2-oxazoles (**I a–f**)



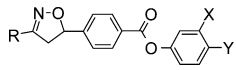
					Transition temperatures/°C					
N	R	X	Y	Yield, %	Cr		SmA	N		I
a	C_4H_9	H	Et	77	●	132	●	–	145	●
b	C_5H_{11}	H	Et	79	●	128	●	–	154	●
c	C_4H_9	F	CN	86	●	107	–	●	138	●
d	C_5H_{11}	F	CN	74	●	92.5	–	●	129	●
e	C_5H_{11}	H	$C_6H_4COOAm^*$	83	●		–	–	220–224	●
f	C_5H_{11}	H	$COOOct^*$	82	●	85	● (SmB)	–	126	●



form only monotropic or thermotropic smectic A phase in a narrow temperature range 107–121°C.

Investigations of the electro-optical and dynamic parameters of LC mixtures containing the cyanoderivatives (**I d**; **II b**, **III c**) have shown that these compounds can be successfully used as components of liquid crystalline mixtures which are characterized by low threshold and saturation voltages in the twisted nematic-effect, by step voltage-contrast characteristics and by low values of switch-on and switch-off times (Table 4).

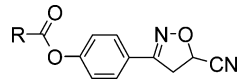
TABLE 2 Yields, Transition Temperatures of 3-alkyl-5-aryl 4,5-dihydro-1,2-oxazoles (**II a–b**)



					Transition temperatures/°C				
N	R	X	Y	Yield, %	Cr	SmA			I
a	C_5H_{11}	H	$C_6H_4COOOct$†	75	●	127†	●	136	●
b	C_5H_{11}	F	CN	82	●		–	53	●

†–Monothropic SmA phase.

TABLE 3 Yields, Transition Temperatures of 3-aryl-5-cyano 4,5-dihydro-1,2-oxazoles (**III a–c**)



			Transition temperatures/°C				
N	R	Yield, %	Cr		SmA		I
a	$C_8H_{17}OC_6H_4$	66	•	86†	•	132	•
b	$C_9H_{19}OC_6H_4$	55	•	87†	•	136.5	•
c	$C_5H_{11}C_6H_{10}$	80	•	107	•	121	•

†–Monothropic SmA phase.

CONCLUSION

The results presented demonstrate that liquid crystalline 3,5-disubstituted 4,5-dihydro-1,2-oxazoles can be used for the development of liquid crystalline materials for nematic display applications with decreased power consumption, step voltage-contrast characteristics and fast response times.

EXPERIMENTAL

Confirmation of the structures of final products was obtained using a GC/MS mass-spectrometer (HP 5972), IR and ^{1}H NMR spectroscopy. Phase

TABLE 4 Physical and Electrooptical Parameters of the Nematic Compositions[a]

Compound	V_{10} (volts)	V_{90} (volts)	P_{10-90}	N_{10-90}	τ_{on} (ms)	τ_{off} (ms)
I d in mixture **A**	2.7	3.6	0.333	12	78	48
I d in mixture **B**	1.46	1.99	0.363	11	29	96
II b in mixture **B**	1.28	1.78	0.390	10	23	78
II b in mixture **A**	2.04	2.80	0.373	11	34	72
III c in mixture **B**	1.67	2.46	0.471	7	36	88

[a]LC mixtures consist 80% of the base mixture and 20% of the compound.

[b]Base mixtures: **A** – 4-ethoxyphenylester of *trans*-4-butylcyclohexane carboxylic acid – 35%, 4-butoxyphenylester of *trans*-4-butylcyclohexane carboxylic acid – 35%, *trans*4-(4-ethoxypheny)-1-propylcyclohexane – 30%.

B–4-pentyl-4-cyanobiphenyl – 35%, 4-octyl-4-cyanobiphenyl – 15%, 4-propoxy-4-cyanobiphenyl – 25%, 4-ethoxyphenylester of *trans*-4-butylcyclohexane carboxylic acid – 20%, 4-cyanobiphenyl ester of *trans*-4-butylcyclohexane carboxylic acid – 5%.

transition temperatures were measured using a Linkam heating stage in conjugation with polarizing PZO microscope and also by differential scanning calorimetry (Setaram DSC 92). The measurements of the electro-optical parameters of the mixtures were performed at room temperature in twisted nematic cells with 6 μm spacers, a polyamide layer was used to obtain homogeneous oriented samples.

General Procedure for the 1,3-Dipolar Cycloaddituon Reaction (Example for III b)

To cooled (−5°C) and stirred solution of corresponding oxime(2.0 g), acrylonitrile (5 ml) and N-chlorosuccinimide (0.8 g) in 35 ml chloroform and 10 ml N,N-dimethylformamide was added 0.85 ml triethylamine during 2 h. The reaction mixture was additionally stirred 2 h at 0°C and 18 h at room temperature, was than acidified with 10% aqueous hydrochloric acid and the organic layer shaken with ether. The ethereal extract was washed with water and dried over anhydrous magnesium sulphate. The solvent was removed in vacuum and the product was crystallized from isopropanol.

Esters **I a–f** and **II a, b** have been synthesized from the corresponding acids and phenols using the following general procedure (example for **I a**): To the mixture of 4-ethylphenol (0.26 g) and 4-(5-butyl-4,5-dihydro-1,2-oxazol-3-yl)benzoic acid (0.5 g) in 15 ml dichloromethane was added 0.42 g dicyclohehylcarbodiimide (DCC) and catalytic amounts of 4-dimethylaminopyridine. Reaction mixture was stirred for 12 h at r. t. and then filtered through the layer of aluminum oxide. The solvent was removed in vacuum and the product was crystallized from isopropanol.

Spectral data for the final compounds **I–III** {IR (samples in $CHCl_3$, ν, cm^{-1}), ^1H NMR (samples in $CDCl_3$, δ, ppm)}:

Ia: 4-(5-Butyl-4,5-dihydro-1,2-oxazol-3-yl)-benzoic acid 4-ethyl-phenyl ester

IR: 3000 (C-$H_{ar.}$), 2945, 2915, 2855 (C-$H_{alk.}$), 1710, 1250, 1065 (COOAr), 1595, 1485(C=$C_{ar.}$). ^1H NMR: 0.88 (3H, t, J 7.2 Hz, CH_3), 1.20 (3H, t, J 7.6 Hz, C**H$_3$**CH_2Ar), 1.28–1.83 (6H, m, CH_2-groups), 2.61 (2H, q, J 7.6 Hz, CH_3C**H$_2$**Ar), 2.92 (1H, dd, J_1 8.4 Hz, J_2 16.8 Hz, 4-CH), 3.36 (1H, dd, J_1 10.4 Hz, J_2 16.8 Hz, 4-CH), 4.66–4.80 (1H, m, 5-CH), 7.05 (2H, d, J 8.8 Hz, arom. H), 7.18 (2H, d, J 8.8 Hz, arom. H), 7.72 (2H, d, J 8.8 Hz, arom. H), 8.14 (2H, d, J 8.8 Hz, arom. H).

Ib: 4-(5-Pentyl-4,5-dihydro-1,2-oxazol-3-yl)-benzoic acid 4-ethyl-phenyl ester

IR: 3015 (C-H_{ar}), 2955, 2925, 2850 (C-$H_{alk.}$), 1725, 1275, 1075 (COOAr), 1600, 1500 (C=$C_{ar.}$). ^1H NMR: 0.86 (3H, t, J 6.5 Hz, CH_3), 1.20 (3H, t, J

7.5 Hz, C**H$_3$**CH$_2$Ar), 1.24–1.80 (8H, m, CH$_2$-groups), 2.60 (2H, q, J 7.5 Hz, CH$_3$C**H$_2$**Ar), 2.94 (1H, dd, J$_1$ 8.5 Hz, J$_2$ 16.5 Hz, 4-CH), 3.36 (1H, dd, J$_1$ 10.5 Hz, J$_2$ 16.5 Hz, 4-CH), 4.66–4.80 (1H, m, 5-CH), 7.06 (2H, d, J 8.5 Hz, arom. H), 7.20 (2H, d, J 8.5 Hz, arom. H), 7.72 (2H, d, J 8.5 Hz, arom. H), 8.14 (2H, d, J 8.5 Hz, arom. H).

Ic: 4-(5-Butyl-4,5-dihydro-1,2-oxazol-3-yl)-benzoic acid 4-cyano-3-fluoro-phenyl ester

IR: 3020, (C-H$_{ar.}$), 2960, 2925, 2860 (C-H$_{alk.}$), 2230 (C≡N), 1740, 1240, 1055 (COOAr), 1600, 1495 (C=C$_{ar.}$). ^{1}H NMR: 0.92 (3H, t, J 7.0 Hz, CH$_3$), 1.28–1.87 (6H, m, CH$_2$-groups), 2.98 (1H, dd, J$_1$ 8.5 Hz, J$_2$ 16.5 Hz, 4-CH), 3.43 (1H, dd, J$_1$ 10.5 Hz, J$_2$ 16.5 Hz, 4-CH), 4.62–4.97 (1H, m, 5-CH), 7.12–7.30 (2H, m, arom. H), 7.70 (1H, dd, J$_1$ 8.5 Hz, J$_2$ 9.0 Hz, arom. H), 7.81 (2H, d, J 8.5 Hz, arom. H), 8.19 (2H, d, J 8.5 Hz, arom. H).

Id: 4-(5-Pentyl-4,5-dihydro-1,2-oxazol-3-yl)-benzoic acid 4-cyano-3-fluoro-phenyl ester

IR: 3025, 3015 (C-H$_{ar.}$), 2960, 2930, 2855 (C-H$_{alk.}$), 2235 (C≡N), 1740, 1245, 1055 (COOAr), 1600, 1500 (C=C$_{ar.}$). ^{1}H NMR: 0.86 (3H, t, J 6.5 Hz, CH$_3$), 1.24–1.80 (8H, m, CH$_2$-группы), 2.95 (1H, dd, J$_1$ 8.5 Hz, J$_2$ 16.5 Hz, 4-CH), 3.38 (1H, dd, J$_1$ 10.5 Hz, J$_2$ 16.5 Hz, 4-CH), 4.66–4.84 (1H, m, 5-CH), 7.12–7.22 (2H, м, arom. H), 7.66 (1H, dd, J$_1$ 8.5 Hz, J$_2$ 9.0 Hz, arom. H), 7.76 (2H, d, J 8.5 Hz, arom. H), 8.13 (2H, d, J 8.5 Hz, arom. H).

Ie: (S)-4-[4-(2-methylbutyloxycarbonyl)phenyl]phenyl 4-(5-pentyl-4,5-dihydro-1,2-oxazolyl)benzoate

IR: 3015 (C-H$_{ar.}$), 2955, 2930, 2870, 2855 (C-H$_{alk.}$), 1730, 1265, 1180 (COOAlk), 1705, 1075 (COOAr), 1600, 1495 (C=C$_{ar.}$). ^{1}H NMR: 0.93 (6H, t, J 6.6 Hz, two CH$_3$-groups), 0.96 (3H, d, J 9.0 Hz, CH$_3$), 1.10–1.90 (11H, m, CH-и CH$_2$-groups), 2.92 (1H, dd, J$_1$ 8.6 Hz, J$_2$ 16.5 Hz, 4-CH), 3.39 (1H, dd, J$_1$ 10.2 Hz, J$_2$ 16.5 Hz, 4-CH), 4.14 (2H, dd, J$_1$ 1.5 Hz, J$_2$ 6.0 Hz, OCH$_2$), 4.54–4.93 (1H, m, 5-CH), 7.26 (2H, d, J 9.8 Hz, arom. H), 7.54–7.80 (6H, m, arom. H), 8.01–8.24 (4H, m, arom. H).

If: (S)-1-methylheptyl 4-[4-(5-pentyl-4,5-dihydro-1,2-oxazolyl)phenylcarbonyloxy]benzoate

IR: 3015, 3005 (C-H$_{ar.}$), 2960, 2930, 2855 (C-H$_{alk.}$), 1735, 1260, 1160 (COOAlk), 1705, 1070 (COOAr), 1600, 1500 (C=C$_{ar.}$). ^{1}H NMR: 0.86 (3H, t, J 6.5 Hz, CH$_3$), 0.90 (3H, t, J 6.5 Hz, CH$_3$), 1.24–1.88 (21H, m, CH$_3$- and CH$_2$-groups), 2.99 (1H, dd, J$_1$ 8.5 Hz, J$_2$ 16.5 Hz, 4-CH), 3.43 (1H, dd, J$_1$ 10.5 Hz, J$_2$ 16.5 Hz, 4-CH), 4.62–4.92 (1H, m, 5-CH), 5.05–5.30

(1H, m, OCH), 7.30 (2H, d, J 8.5 Hz, arom. H), 7.80 (2H, d, J 8.5 Hz, arom. H), 8.11 (2H, d, J 8.5 Hz, arom. H), 8.22 (2H, d, J 8.5 Hz, arom. H).

IIa: (S)-4′ -[4-(3-Pentyl-4,5-dihydro-isoxazol-5-yl)-benzoyloxy]-biphenyl-4-carboxylic acid 1-methyl-heptyl ester

IR: 3020 (C=$H_{ar.}$), 2955, 2925, 2850 (C-$H_{alk.}$), 1725 (COOOct*), 1700, 1255, 1060 (COOAr), 1600, 1495 (C=$C_{ar.}$). ^{1}H NMR: 0.87 (3H, t, J 6.3 Hz, CH_3), 0.88 (3H, t, J 6.3 Hz, CH_3), 1.20–1.75 (19H, m, CH_3- and CH_2-groups), 2.39 (2H, t, J 7.7 Hz, 3′-CH_2), 2.87 (1H, dd, J_1 7.7 Hz, J_2 16.5 Hz, 4-CH), 3.45 (1H, dd, J_1 10.7 Hz, J_2 16.5 Hz, 4-CH), 5.17 (1H, m, O−CH), 5.63 (1H, dd, J_1 7.7 Hz, J_2 10.7 Hz, 5-CH), 7.30 (2H, d, J 8.7 Hz, arom. H), 7.48 (2H, d, J 8.2 Hz, arom. H), 7.61 (2H, d, J 2.7 Hz, arom. H), 7.69 (2H, d, J 2.7 Hz, arom. H), 8.11 (2H, d, J 8.7 Hz, arom. H), 8.20 (2H, d, J 8.2 Hz, arom. H).

IIb: 4-(3-Pentyl-4,5-dihydro-1,2-oxazol-5-yl)-benzoic acid 4-cyano-3-fluoro-phenyl ester

IR: 3020, (C-$H_{ar.}$), 2960, 2935, 2865 (C-$H_{alk.}$), 2230 (C≡N), 1740, 1250, 1055 (COOAr), 1600, 1495 (C=$C_{ar.}$). ^{1}H NMR: 0.89 (3H, t, J 6.3 Hz, CH_3), 1.20–1.68 (6H, m, CH_2-groups), 2.38 (2H, t, J 7.7 Hz, 3′-CH_2), 2.85 (1H, dd, J_1 7.7 Hz, J_2 16.5 Hz, 4-CH), 3.46 (1H, dd, J_1 10.7 Hz, J_2 16.5 Hz, 4-CH), 5.63 (1H, dd, J_1 7.7 Hz, J_2 10.7 Hz, 5-CH), 7.20 (2H, d, J 10.4 Hz, arom. H), 7.49 (2H, d, J 9.5 Hz, arom. H), 7.70 (1H, t, J 9.5 Hz, arom. H), 8.17 (2H, d, J 10.4 Hz, arom. H).

IIIa: 4-Octyloxy-benzoic acid 4-(5-cyano-4,5-dihydro-1,2-oxazol-3-yl)-phenyl ester

IR: 3005 (C-$H_{ar.}$), 2920, 2850 (C−$H_{alk.}$), 1730, 1255, 1065 (COOAr), 1600, 1500 (C−$C_{ar.}$), 1165 (C=O). ^{1}H NMR: 0.87 (3H, t, J 4.5 Hz, CH_3), 1.15–1.90 (14H, m, CH_2-groups), 3.67 (2H, d, J 8.3 Hz, 4-CH_2), 3.98 (2H, t, J 6.3 Hz, OCH_2), 5.31 (1H, t, J 8.3 Hz, 5-CH), 6.91 (2H, d, J 9.0 Hz, arom. H), 7.24 (2H, d, J 9.0 Hz, arom. H), 7.66 (2H, d, J 9.0 Hz, arom. H), 8.07 (2H, d, J 9.0 Hz, arom. H).

IIIb: 4-Nonyloxy-benzoic acid 4-(5-cyano-4,5-dihydro-1,2-oxazol-3-yl)-phenyl ester

IR: 3005 (C-$H_{ar.}$), 2925, 2850 (C−$H_{alk.}$), 1720, 1245, 1065 (COOAr), 1600, 1500 (C−$C_{ar.}$), 1165 (C=O). ^{1}H NMR: 0.83 (3H, t, J 4.5 Hz, CH_3), 1.15–1.90 (16H, m, CH_2-groups), 3.68 (2H, d, J 8.3 Hz, 4-CH_2), 3.98 (2H, t, J 6.3 Hz, OCH_2), 5.32 (1H, t, J 8.3 Hz, 5-CH), 6.91 (2H, d, J 9.0 Hz, arom. H), 7.24 (2H, d, J 9.0 Hz, arom. H), 7.66 (2H, d, J 9.0 Hz, arom. H), 8.07 (2H, d, J 9.0 Hz, arom. H).

IIIc: 4-Pentyl-cyclohexanecarboxylic acid 4-(5-cyano-4,5-dihydro-1,2-oxazol-3-yl)-phenyl ester

IR: 3020, ($C\text{-}H_{ar.}$), 2960, 2930, 2855 ($C\text{-}H_{alk.}$), 1740, 1160, 1115 (COOAr), 1600, 1505 ($C{=}C_{ar.}$). ^{1}H NMR: 0.88 (3H, t, J 5.8 Hz, CH_3), 1.14–1.38 (10H, m, CH_2-groups), 1.43–2.35 (7H, m, CH- and CH_2-groups), 2.48 (1H, tt, J_1 3.4 Hz, J_2 11.9 Hz, CHCOO), 3.70 (1H, d, J 7.0 Hz, 4-CH), 3.71 (1H, d, J 8.9 Hz, 4-CH), 5.35 (1H, dd, J_1 7.0 Hz, J_2 8.9 Hz, 5-CH), 7.14 (2H, d, J 8.8 Hz, arom. H), 7.66 (2H, d, J 8.8 Hz, arom. H).

REFERENCES

[1] Brettle, R., Dunmur, D. A., Marson, C. M., Pinol, M., & Toriyama, K. (1993). *Liq. Cryst.*, *13*, 515.
[2] Iglesisas, R., Serrano, J. L., & Sierra, T. (1997). *Liq. Cryst.*, *22*, 37.
[3] Friedman, M. R., Toyne, K. J., Goodby, J. W., & Hird, M. (2001). *Liq. Cryst.*, *28*, 901.
[4] Vill, V. (1999). *LiqCryst Database of Liquid Crystalline Compounds for Personal Computers*, LCI Publisher GmbH: Hamburg.
[5] Bezborodov, V. S., Lee, C. J., & Uh, K. H. (1997). 6th International Conference on Ferroelectric Liquid Crystals. Conference Summaries. Brest, France. 152.