



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 18 Oct 2010

To cite this article: Vladimir F. Petrov & Assya I. Pavluchenko (2002): Study of Some Liquid Crystalline 2,5-Disubstituted Pyridine Derivatives, *Molecular Crystals and Liquid Crystals*, 383:1, 63-79

To link to this article: <http://dx.doi.org/10.1080/713738765>

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STUDY OF SOME LIQUID CRYSTALLINE 2,5-DISUBSTITUTED PYRIDINE DERIVATIVES

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The physico-chemical properties of some liquid crystalline 2,5-disubstituted pyridine derivatives have been studied with the establishment of their structure-property relationships. The results of this work have been compared with those of the corresponding reference compounds. Some of the presented 2,5-disubstituted derivatives can be considered as the suitable components of liquid crystal materials for display applications.

Keywords: liquid crystalline 2,5-disubstituted pyridine derivatives, physico-chemical properties

INTRODUCTION

In continuation of our work on the study of physico-chemical properties of liquid crystalline 2,5-disubstituted pyridine derivatives [1–11], the effect of the introduction of the pyridin-2,5-diyl fragment into the molecular core of some liquid crystals will be investigated, rationalized in terms of existent theories, and compared with other well-known molecular fragments.

EXPERIMENTAL TECHNIQUES

The static dielectric constants ϵ_{\perp} and ϵ_{\parallel} of the liquid crystalline derivatives were determined from the complex impedance of a parallel plate capacitor comprising the magnetic field-aligned liquid crystals as a dielectric [6]. The refractive indices n_o and n_e were measured at the wavelength $\lambda = 589 \text{ nm}$ in an Abbe refractrometer using a homogeneously surface-aligned prism. The kinematic viscosity ν was determined with an Ostwald-type viscosimeter [6].

RESULTS AND DISCUSSION

Mesomorphic Properties

The measurement of the phase transition temperatures of presented compounds has been reported earlier [1–9,12]. Here we discuss their mesomorphic properties, which are important for better understanding their physico-chemical properties measured in the mesophases.


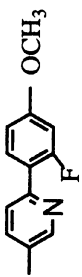
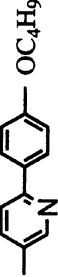



It is evident from Tables 1 and 3 that two-ring alkyl-alkoxy and dialkyl phenylpyridines with short substituents usually exhibit the monotropic nematic (compound **1-1**) or smectic (compound **3-2**) phases. Increasing the length of the alkyl and alkoxy groups results in more pronounced appearance of the mesophases (compound **1-3**). Changing the position of the nitrogen atom in the pyridine ring of compound **1-3** to obtain compound **2-4** (Table 2) results in the disappearance of the nematic phase, a slight decrease in the melting point, and the creation of only smectic phase with a higher clearing point. Similar effects have been observed for other 2,5-disubstituted pyridine derivatives [9].

The introduction of the pyridine ring into the molecular core of two-ring 1,4-disubstituted cyclohexenylene (compounds **1-4** and **1-5**, Table 1) and trans-1,4-cyclohexylene (compounds **1-7** to **1-10**, Table 1) dialkyl derivatives do not create the mesophases. Increasing the length of the alkyl chain may introduce the monotropic nematic phase in the former compounds (compound **1-6**).

The data presented in Table 3 reveal that the introduction of the sulphur atom into the alkyl chain of two-ring pyridin-2,5-diyl derivatives leads to the disappearance of the mesophases and increases the melting points (compounds **3-1** and **3-2**, **3-3** and **3-4**). In the case of three-ring derivatives such an introduction slightly lowers the melting temperature, significantly enhances the smectic thermostability, and lowers the clearing point in comparison with those of the corresponding alkyl derivative (compounds **3-5** and **3-6**). The reduction in the clearing temperatures can be explained by a lower conformational mobility of the alkylthia chain in comparison with that of the alkyl chain [25–27]. The lower rotation barrier around the carbon-sulphur bond relative to the carbon-carbon bond [26] leads to the formation of the *trans-gauche* conformers [27], which increase the disorder of the system [25].

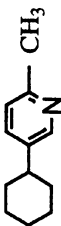
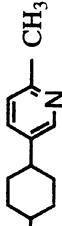

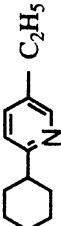
As can be seen from Table 3, the replacement of the *n*-propyl group by (*E*) 2-propenyl chain in compound **3-11** to obtain compound **3-12** results in a significant increase of the melting temperature and lowering the nematic-isotropic phase transition temperature. Similar effects have been recorded for other alkenyl derivatives [4,10,28–31].

TABLE 1 Physico-Chemical Properties of Some Liquid Crystals

No.	Compound	Phase Transitions, °C	ϵ_{\perp}	$\Delta\epsilon$	$\Delta\epsilon/\epsilon_{\perp}$	Δn^a	v , mm^2s^{-1}	Ref.
1-1		Cr 41.5 N (32) I		-0.64 ^a		0.152	20.0 ^a	[1]
1-2		Cr 25.3 I		-0.44 ^a		0.132	25.0 ^a	[2]
1-3		Cr 50 Sm 54 N 61 I	4.55 ^b	-0.65 ^b	-0.14 ^b			[3]
1-4		Cr < 20 I					18.0 ^c ; 10.7 ^d	[4]
1-5		Cr < 20 I					19.7 ^c ; 12.0 ^d	[4]
1-6		Cr 24.9 N (24.6) I					32.1 ^c ; 21.0 ^d	[4]

(Continued)

TABLE 1 (Continued)

No.	Compound	Phase Transitions, °C	ϵ_{\perp}	$\Delta\epsilon$	$\Delta\epsilon/\epsilon_{\perp}$	Δn^a	v , mm ² s ⁻¹	Ref.
1-7		Cr < 20 I					10.5 ^d	[12]
1-8		Cr < 20 I					11.8 ^d	[12]
1-9		Cr < 20 I					20.6 ^d	[12]
1-10		Cr < 20 I					7.0 ^c ; 4.4 ^d	[12]

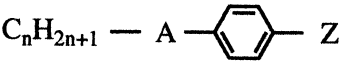
^aExtrapolated from the 10 wt% solution in ZLI-3086 at 20°C.















^b $\tau = T_{\text{meas}}/T_{N-I} = 0.95$, T_{meas}/T_{N-I} , K.

^c $T_{\text{meas}} = 20^{\circ}\text{C}$.

^d $T_{\text{meas}} = 35^{\circ}\text{C}$.

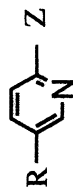
TABLE 2 Physico-Chemical Properties of Liquid Crystals:



No.	<i>n</i>	A	Z	Phase Transitions, °C	Δε	Δ <i>n</i> ^a	<i>v</i> mm ² s ⁻¹	Ref.
2-1	5		OCH ₃	Cr 41 N (31) I	-0.50 ^a	0.090	8.0 ^a	[13]
2-2	5		OCH ₃	Cr 38 Sm (23.5) SmA (31.2) I				[14]
2-3	5		OCH ₃	Cr 64 N 70 I				[15]
2-4	6		OC ₄ H ₉	Cr 48 Sm 85 I				[3]
2-5	6		OC ₄ H ₉	Cr 20.8 Sm 54.5 SmA 83.4 I				[14]
2-6	6		OC ₄ H ₉	Cr 40 SmB 78 I				[16]
2-7	6		OC ₄ H ₉	Cr 40 N 53 I				[17]
2-8	6		OC ₄ H ₉	Cr 35.5 SmA 44 N 50 I				[18]
2-9	6		OC ₄ H ₉	Cr 55 I				[19]
2-10	6		OC ₄ H ₉	Cr 55 N (44) I				[20]
2-11	6		OC ₄ H ₉	Cr 48 SmA 88 I				[21]
2-12	6		OC ₄ H ₉	Cr 49 SmC (43) N 57 I				[22]
2-13	5		CH ₃	Cr 25 N(-4) I			7.0 ^b	[23]
2-14	4		C ₂ H ₅	Cr < 20 I				[24]

^aExtrapolated from the 10 wt% solution in ZLI-1132 at 20°C.

^bExtrapolated value.

TABLE 3 Physico-Chemical Properties of Some Liquid Crystals: 

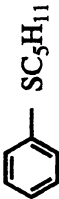

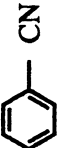
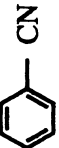
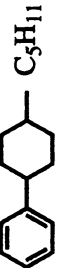
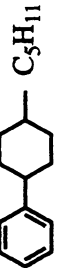

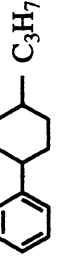
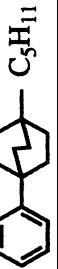
No.	R	Z	Phase Transitions, °C	$\Delta\epsilon^a$	Δn^a	Ref.
3-1	C ₃ H ₇		Cr 40.5 I			[1]
3-2	C ₃ H ₇		Cr 20 Sm (5) I			[5]
3-3	CH ₃ SCH ₂		Cr 78 I			[1]
3-4	C ₂ H ₅		Cr 69.3 N (35.7) I			[6]
3-5	CH ₃ SCH ₂		Cr 64 Sm 86 N 148.5 I			[1]
3-6	C ₂ H ₅		Cr 65.8 Sm 78 N 168 I			[4]
3-7	C ₅ H ₁₁		Cr 109 N 165.1 I	-0.16	0.192	[1]
3-8	C ₅ H ₁₁		Cr 48 Sm 93.8 N 177.4 I			[4]
3-9	C ₃ H ₇		Cr 113 Sm 121 N 225 I	-0.14	0.190	[7]

TABLE 3 (Continued)

No.	R	Z	Phase Transitions, °C	$\Delta\epsilon^a$	Δn^a	Ref.
3-10	C ₃ H ₇		Cr 37 Sm 93.5 N 179 I	-0.24	0.192	[4]
3-11	C ₃ H ₇		Cr 15 N 111 I	-0.46	0.154	[8]
3-12	CH ₂ =CHCH ₂		Cr 53 N 83.2 I		0.148	[8]
3-13	C ₃ H ₇		Cr 66 N 151 I	-0.44		[4]
3-14	C ₃ H ₇		Sm 116 N 147 I		0.162	[4]
3-15	C ₃ H ₇		Cr 47 N 145 I	-0.02		[1]
3-16	C ₅ H ₁₁		Cr 40.2 Sm 84.6 N 153.1 I			[4]
3-17	C ₄ H ₉		Cr 119 Sm 219 N 231 I		0.178	[8]

^aExtrapolated from the 10 wt% solution in ZLI-3086 at 20°C. A = NH₂.







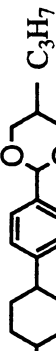
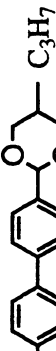
The effect of changing the position of the pyridine ring in the molecular core of three-ring derivatives on their mesomorphic behavior is well illustrated by comparing the phase transition temperatures of compounds **3-10** and **4-4** (Tables 3 and 4), with broad nematic range and low melting point observed for the former derivative and highly smectic character and slightly enhanced clearing point recorded for the latter compound.

It is evident from Tables 1, 3, 4 and 5 that the lateral substitution of the 2,5-disubstituted pyridine derivatives by the fluorine, methyl, and amino groups lowers (compounds **1-1** and **1-2**; **3-10** and **3-11**; **4-1** and **4-3**; **5-1** and **5-2**) and enhances (compounds **3-10** and **3-13**; **4-1** and **4-2**) the melting temperatures, lowers the nematic (compounds **3-10** and **3-11**; **3-13**, **3-14**; **4-1** and **4-2**, **4-3**; **5-1** and **5-2**) and smectic (compounds **4-1** and **4-2**) thermostabilities, increases the smectic thermostability (compounds **3-10** and **3-14**), and results in the disappearance of the nematic (compounds **1-1** and **1-2**) and smectic (compounds **3-10** and **3-11**, **3-13**; **5-1** and **5-2**) mesophases. The lateral hydroxy substitution results in high melting point, and smectic and nematic thermostabilities caused by the formation of the hydrogen bonds (compound **3-17**). These findings reveal the importance of the structure of the pyridin-2,5-diyl derivatives and the lateral substituents on their mesomorphic properties. Similar effects have been observed for other derivatives (compare for example, compounds **4-5** and **4-10** in Table 4) and explained in terms of reducing the intermolecular forces due to the broadening the molecules by the lateral groups [39].

As can be seen from Tables 3 and 5, the introduction of the ester group into the molecular core of three-ring compound **3-16** to create compound **5-5** results in the significant increase of the melting and clearing points and the formation of only nematic phase with a lower nematic range. These effects are due to the increased conjugation length of the π -electron system, and consequently the enhanced molecular polarizability and inter- and intramolecular interactions, which in turn result in more effective molecular packing for the formation of the nematic phase. While the introduction of the ethylene linkage into the molecular core of three-ring pyridine derivatives leads to the formation of the smectic and nematic phases with moderate thermostabilities (compounds **5-3**, **5-4**, Table 5) which can be explained in terms of increased molecular flexibility and, consequently, broadening the molecule and reduction of the intermolecular forces [40].

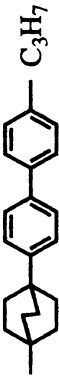

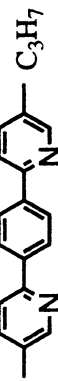

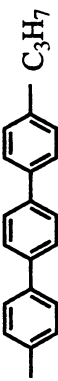
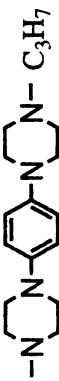
The replacement of the reference fragments, such as 1,4-phenylene, *trans*-1,4-cyclohexylene, *trans*-1,3-dioxan-2,5-diyl, and others by the pyridin-2,5-diyl in two- and three-ring derivatives presented in Tables 1–4 increases (compounds **1-1**, **2-1** and **2-2**; **1-3** and **2-5** to **2-8**, **2-11**, **2-12**; **3-7** and **4-7**, **4-8**; **3-10** and **4-5**) and lowers (compounds **1-1** and **2-3**; **1-3** and **2-9**, **2-10**; **1-8** and **2-13**; **3-9** and **4-9**; **3-10** and **4-6**, **4-7**; **3-11** and **4-10**) the melting temperatures, lowers (compounds **1-1** and **2-3**; **1-3** and **2-4** to

TABLE 4 Physico-Chemical Properties of Some Liquid Crystals

No.	Compound	Phase Transitions, °C	$\Delta\epsilon^a$	Δn^a	Ref.
4-1		Cr 87 Sm 142 N 208 I	-0.44	0.192	[7]
4-2		Cr 94 Sm 138.8 N 179.8 I	-0.84	0.176	[9]
4-3		Cr 45.2 N 174.5 I	-0.24	0.176	[9]
4-4		Cr 48 SmB 163 SmA 184 N 185 I	-0.22	0.190	[32]
4-5		Cr 29 Sm 160 N 170 I	+0.34	0.192	[33]
4-6		Cr 101 N 187 I			[34]
4-7		Cr ₂ 45.3 Cr ₁ 72.4 N 157.3 I			[35]
4-8		Cr 85.4 Sm (80.5) SmB 86.2 N 162.9 I			[35]

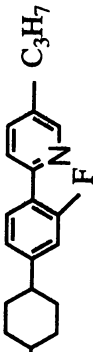

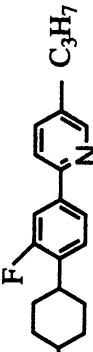



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TABLE 4 (Continued)

No.	Compound	Phase Transitions, °C	$\Delta\epsilon^a$	Δn^a	Ref.
4-9		Cr 175 SmB 191 N 210 I			[15]
4-10		Cr 20 Sm 43.5 N 98.5 I			[36]
4-11		Cr 183 N 208 I			[7]
4-12		Cr 185 N 213 I			[37]
4-13		Cr 221 Sm 228 I			[38]
4-14		Cr 163.3 SmB 171.5 I			[14]

^aExtrapolated from the 10 wt% solution in ZLI-3086 at 20°C.

TABLE 5 Physico-Chemical Properties of Some Liquid Crystals

No.	Compound	Phase Transitions, °C	ϵ_{\perp}	$\Delta\epsilon$	$\Delta\epsilon/\epsilon_{\perp}$	ΔT	Ref.
3-15		Cr 47 N 145 I	2.96	-0.01	-0.003	60	[1]
5-1		Cr 51 Sm 94 N 157.8 I	3.62	-0.23	-0.064	60	[5]
5-2		Cr 47.6 N 127.5 I	3.40	-0.40	-0.118	78	[4]
5-3		Cr 48 Sm 61 N 93 I	4.22	-0.33	-0.078	20	[8]
5-4		Cr 73.1 Sm 82.4 N 133.5 I	3.35	-0.04	-0.012	30	[12]
5-5		Cr 116 N 173.5 I	3.90	-0.49	-0.126	50	[12]

$$\Delta T = T_{N-I} - T_{meas} \text{ } ^{\circ}\text{C.}$$

2-6, **2-11**; **3-10** and **4-6**) and increases (compounds **1-1** and **2-1**, **2-2**; **1-3** and **2-7**, **2-8**, **2-10**, **2-12**; **3-7** and **4-7**, **4-8**; **3-9** and **4-9**; **3-10** and **4-5**; **3-11** and **4-10**; **4-4** and **4-5**) the clearing points, introduces the smectic (compounds **1-3** and **2-9**; **3-10** and **4-6**) and nematic mesophases (compounds **1-3** and **2-5**, **2-9**, **2-11**), and results in the disappearance of the nematic (compounds **1-8** and **2-13**) and smectic phases (compounds **1-1** and **2-2**; **3-7** and **4-8**; **3-11** and **4-10**). Such replacements lower (compounds **1-3** and **2-7**, **2-12**; **3-7** and **4-7**, **4-8**; **3-10** and **4-6**) and increase (compounds **1-3** and **2-8**; **3-9** and **4-9**; **3-10** and **4-5**; **3-11** and **4-10**) the nematic ranges.

The introduction of two pyridin-2,5-diyl fragments into the molecular core of three-ring derivatives creates only nematic phase with high melting and clearing points (compound **4-11**, Table 4) that are slightly lower than those of the corresponding pyrimidin-2,5-diyl derivative (compound **4-12**), which also exhibit only nematic phase.

Other corresponding reference compounds **4-13** and **4-14** show only smectic phases with higher and lower melting and clearing temperatures, respectively.

Interestingly, the replacement of the *trans*-1,3-dioxan-2,5-diyl by the *trans*-1,4-cyclohexylene in compound **3-7** to obtain compound **3-8** lowers the melting point, introduces the smectic phase and increases the nematic thermostability. While the replacement of the 1,4-bicyclo[2.2.2] octylene by the *trans*-1,4-cyclohexylene in compound **3-9** to create compound **3-10** lowers the melting point, smectic, and nematic thermostabilities. Similar results have been observed for other *trans*-1,4-cyclohexylene derivatives [41].

The presented results reveal the importance of the molecular structure of the 2,5-disubstituted pyridine derivatives, the position and quantity of their pyridine rings, and position of the nitrogen in the pyridine ring on their mesomorphic properties. Indeed, the geometrical and electronic structure of the pyridine ring [42–46] plays a crucial role in the intra- and inter-molecular interactions which affect the packing of the molecules which predominantly influences mesophase stability [47–49]. Similar results have been reported for other liquid crystalline pyridine derivatives [5,7,9].

Static Dielectric Properties

The relationship between the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, where ϵ_{\parallel} and ϵ_{\perp} are, respectively, dielectric constants, that are parallel and perpendicular to the nematic director \mathbf{n} ; and molecular structure of liquid crystals is described by the theory of Maier and Meier [50]:

$$\Delta\epsilon = NhF/\epsilon_0[\Delta\alpha - F\mu^2/kT(1 - 3\cos^2\beta)]S, \quad (1)$$

where $h = 3\epsilon^*/(2\epsilon^* + 1)$, $\epsilon^* = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$, $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the polarizability anisotropy, F is the cavity reaction field, μ is the dipole moment, β is the angle between the molecular long axis and the dipole moment, N is the number of molecules per unit volume, and S is the order parameter.

It has been shown that meaningful comparisons of the dielectric (as well as optical and elastic) properties of liquid crystals with different nematic-isotropic phase transition temperatures T_{N-I} can only be made at constant reduced temperature $\tau = T_{\text{meas}}/T_{N-I}$ [51].

Tables 1–5 present some data on the dielectric properties of liquid crystalline compounds measured at a constant reduced temperature and extrapolated from the liquid crystalline mixtures at 20°C. According to Schadt [51], the extrapolations are not meaningful; however, these estimations are only one way to obtain a rough definition of the dielectric (as well as optical and elastic) properties of nonmesomorphic compounds, smectic liquid crystals, and liquid crystals with narrow nematic range.

It is evident from Tables 1, 3, 4, and 5 that two- and three-ring dialkyl and alkyl-alkoxy substituted pyridin-2,5-diyl derivatives exhibit the negative values of the dielectric anisotropy, which are due to the a larger contribution of the dipole moment of the pyridine ring $\{\mu = 2.35 \text{ D}$ [42]] to the perpendicular component ϵ_{\perp} in comparison with that to the parallel component ϵ_{\parallel} (compounds **1-1**, **1-3**, **3-7**, **3-9** to **3-11**, **3-13**, **3-15**, **4-1** to **4-5**, **5-1** to **5-5**). Lateral fluoro and methyl substitutions affect the value of $\Delta\epsilon$ of the pyridine derivatives in different degrees depending on their positions, the position of the pyridine ring, and existence of the terminal alkyl or alkoxy groups. It should be pointed out that for the given molecular structures of the 2,5-disubstituted pyridine derivatives their lateral fluoro and methyl substitutions do not change the negative sign of the dielectric anisotropy (compounds **1-1** and **1-2**; **3-10** and **3-11**, **3-13**; **5-1** and **5-2**). The replacement of the pyridin-2,5-diyl by the *trans*-1,4-cyclohexylene lowers the dielectric anisotropy (in absolute value) due to the contribution to the perpendicular component of the total dipole moment and anisotropy of the polarizability being decreased [42,43,52,53] (compounds **1-1** and **2-1**; Tables 1 and 2). This effect is more pronounced for the three-ring dialkyl derivatives, resulting in the change of the negative to the positive sign of the dielectric anisotropy (compounds **4-4** and **4-5**; Table 4). The presented results are found to be in agreement with Equation (1) [50].

It is evident from Tables 1 and 5 that the 2,5-disubstituted pyridine derivatives (compounds **1-3**, **3-15**, **5-1** to **5-5**) exhibit low values (< 1) of the ratio $\Delta\epsilon/\epsilon_{\perp}$ which are favorable for supertwisted nematic display applications [51]. Similar trends have been demonstrated for other pyridine derivatives [9].

Optical Properties

The phenomenological relation between the refractive index and the electric polarization is defined as [54,55]:

$$(n^{*2} - 1)/(n^{*2} + 2) = N\alpha^*/3\epsilon_0, \quad (2)$$

where the mean polarizability $\alpha^* = (\alpha_{\parallel} + 2\alpha_{\perp})/3$, the mean refractive index $n^{*2} = (n_e^2 + 2n_o^2)/3$, and n_o is the ordinary and n_e the extraordinary refractive indices. From Equation (2) and the previous section it follows that the pyridine derivatives which have large induced polarizability of their highly conjugated π -electron [42,43,52] system exhibit the optical anisotropy $\Delta n = n_e - n_o$, which is much larger than that of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives (compounds **1-1** and **2-1**). The replacement of the 1,4-phenylene by the pyridin-2,5-diyl gives very similar values of the optical anisotropy (compounds **4-4** and **4-5**), reflecting the small difference in the polarizability of the pyridine and benzene [42,43,56]. Similar results have been found for other pyridine derivatives presented in Tables 3 and 4 (compounds **3-7**, **3-9**, **3-10**, **4-1**).

The data presented in Table 3 reveal that the (*E*) 2-alkenylation of the three-ring 2,5-disubstituted pyridine derivative slightly lowers the value of the optical anisotropy compared with that of the corresponding alkyl derivative (compounds **3-11** and **3-12**). Similar trends have been reported for other alkenyl derivatives [10,28–31].

Lateral fluoro, methyl, and amino substitution of the pyridine derivatives lowers their optical anisotropy in comparison with that of the corresponding parent compounds (compounds **1-1** and **1-2**; **3-10** and **3-11**, **3-14**; **4-1** and **4-2**, **4-3**; Tables 1, 3, and 4). Similar value of Δn has been received for lateral hydroxy substituted derivative **3-17**. This can be explained in terms of reducing the effective conjugation length of the π -electron system, resulting in a shorter resonance wavelength of the UV absorption spectrum (for laterally fluoro substituted liquid crystals, it has been shown in Khoo and Wu [57]).

Viscosity

It has been shown that the nematic liquid crystalline materials for display applications should have a low viscosity for giving the acceptable response times to LCDs [51,58]. According to the results of the kinematic viscosity ν presented in Tables 1 and 2, the 2,5-disubstituted pyridine derivatives exhibit higher values of the kinematic viscosity compared with those of corresponding *trans*-1,4-cyclohexylene, and 1,4-phenylene disubstituted derivatives (compounds **1-1** and **2-1**, **1-8** and **2-13**). As can be seen from Table 1, lateral fluoro substitution increases the value of the viscosity

(compounds **1-1** and **1-2**). Interestingly, the replacement of the 1,4-cyclohexenylene by the *trans*-1,4-cyclohexylene lowers the kinematic viscosity (compounds **1-5** and **1-7**; Table 1). Increasing the length of the alkyl chains in these derivatives enhances the viscosity (compounds **1-4** to **1-6**, **1-7** to **1-9**; Table 1). Changing the position of the nitrogen atom in the pyridine ring significantly affects the kinematic viscosity of the pyridine derivatives (approximate comparison of compounds **1-7** and **1-10**). Similar results have been found for other liquid crystalline derivatives [9,39,41].

CONCLUSION

The presented results show the dependence of the physico-chemical properties of 2,5-disubstituted pyridine derivatives on their molecular structure including the quantity and position of the pyridine rings and the position of the nitrogen atom in these rings. A comparison with the corresponding reference derivatives has been made. It is believed that the results of this study will broaden the understanding of fundamental structure-property relationships in liquid crystals.

REFERENCES

- [1] A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, and E. P. Pozhidaev, *14th Int. Liq. Cryst. Conf.*, June 21–26, University of Pisa, Pisa, Italy, Presentation A-P51, (1992).
- [2] R. Buchecker, A. I. Pavluchenko, V. F. Petrov, M. Schadt, N. I. Smirnova, and V. V. Titov, *Eur. Pat. Appl.*, EP 0361 157, (1990).
- [3] A. I. Pavluchenko, V. V. Titov, and N. I. Smirnova, *Advances in Liquid Crystal Research and Applications*, L. Bata (ed.) (Pergamon Press-Akademiai Kiado, Oxford-Budapest, 1980), p. 1007.
- [4] A. I. Pavluchenko, G. V. Purvanyatskas, N. I. Smirnova, M. F. Grebenkin, V. F. Petrov, M. I. Barnik, A. V. Ivaschenko, N. I. Korotkova, E. I. Kovshev, A. Z. Rabinovich, N. A. Bumagin, N. P. Andriukhova, I. P. Beletskaya, S. D. Maltsev, and V. V. Titov, *PCT WO 88/07992*, (1988).
- [5] V. F. Petrov, A. I. Pavluchenko, and N. I. Smirnova, *Mol. Cryst. Liq. Cryst.*, **265**, 47 (1995).
- [6] M. F. Grebyonkin, V. F. Petrov, V. V. Belyaev, A. I. Pavluchenko, N. I. Smirnova, E. I. Kovshev, V. V. Titov, and A. V. Ivashchenko, *Mol. Cryst. Liq. Cryst.*, **129**, 245 (1985).
- [7] A. I. Pavluchenko, V. F. Petrov, and S. Takenaka, *IDW98, Proc. Fifth Int. Display Workshops*, December 7–9, Kobe, Japan, (1998), p. 835.
- [8] A. I. Pavluchenko, V. F. Petrov, M. F. Grebenkin, A. V. Ivaschenko, N. I. Korotkova, N. I. Smirnova, L. V. Krjuchkova, L. A. Karamysheva, I. F. Agafonova, P. P. Dakhnov, R. Kh., Geivandov, E. P. Pozhidaev, and B. M. Bolotin, *Eur. Pat. Appl.*, EP 0 374 849, (1989).
- [9] A. I. Pavluchenko, V. F. Petrov, and N. I. Smirnova, *Liq. Cryst.*, **19**, 811 (1995).
- [10] A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, M. F. Grebyonkin, and V. V. Titov, *Mol. Cryst. Liq. Cryst.*, **209**, 155 (1991).

- [11] A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, Yu. A. Fialkov, S. V. Shelyazhenko, and L. M. Yagupolsky, *Mol. Cryst. Liq. Cryst.*, **209**, 225 (1991).
- [12] A. I. Pavluchenko, N. I. Smirnova, L. V. Kryuchkova, and V. F. Petrov, Russian Patent SU 1 749 219 (1992).
- [13] U. Finkenzeller, H.-A. Kurneier, and E. Poetsch, 18 Freiburger Arbeitstagung Flussigkristalle, P 17, (1989).
- [14] K. Kinashi, S. Takenaka, and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, **67**, 49 (1981).
- [15] N. Carr, G. W. Gray, and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, **129**, 301 (1985).
- [16] L. A. Karamysheva, E. I. Kovshev, A. I. Pavluchenko, K. V. Roitman, V. V. Titov, S. I. Torgova, and M. F. Grebenkin, *Mol. Cryst. Liq. Cryst.*, **67**, 241 (1981).
- [17] H. Zaschke, *J. Prakt. Chem.*, **317**, 617 (1975).
- [18] H.-M. Vorbrodt, S. Deresch, H. Kresse, A. Wiegeleben, D. Demus, and H. Zaschke, *J. Prakt. Chem.*, **323**, 902 (1981).
- [19] Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **58**, 1821 (1985).
- [20] Y. Haramoto, A. Nobe, and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **57**, 1966 (1984).
- [21] J. Hanna, K. Kogo, and K. Kafuku, Eur. Pat. Appl., EP 0 864 631, 1998.
- [22] D. Demus, B. Krucke, F. Kuschel, H. U. Nothnack, G. Pelzl, and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, **56**, 115 (1979).
- [23] V. Vill, *LiqCryst.* 4.0 (2001).
- [24] R. Eidenschink, J. Krause, and L. Pohl, Ger. Pat. Appl., DE 2 636 684 (1978).
- [25] E. Dalcanele, C. Arena, M. Catellani, and G. P. Chiusoli, *Liq. Cryst.*, **12**, 905 (1992).
- [26] C. H. Bushweller and M. H. Gianni, *The Chemistry of Ethers, Hydroxyl Groups and their Sulphur Analogues*, S. Patai (ed.) (John Wiley & Sons, New York, 1980), Chap. 5.
- [27] N. L. Allinger and M. J. Hickey, *J. Am. Chem. Soc.*, **97**, 5167 (1975).
- [28] M. Schadt, M. Petrzilka, P. R. Gerber, and A. Villiger, *Mol. Cryst. Liq. Cryst.*, **122**, 241 (1985).
- [29] M. Schadt, R. Buchecker, F. Leenhouts, A. Boller, A. Villiger, and M. Petrzilka, *Mol. Cryst. Liq. Cryst.*, **139**, 1 (1986).
- [30] R. Buchecker and M. Schadt, *Mol. Cryst. Liq. Cryst.*, **149**, 359 (1987).
- [31] M. Schadt, R. Buchecker, and K. Muller, *Liq. Cryst.*, **5**, 293 (1989).
- [32] M. P. Burrow, G. W. Gray, D. Lacey, and K. J. Toyne, *Liq. Cryst.*, **3**, 1643 (1988).
- [33] A. V. Ivaschenko, S. I. Torgova, L. A. Karamysheva, and A. G. Abolin, *Liq. Cryst.*, **7**, 475 (1990).
- [34] K. J. Toyne, M. Hird, S. Greenfield, and E. Poetsch, *Eur. Pat. Appl.*, EP 0 354 434 (1989).
- [35] J. Szulc, K. Czuprynski, R. Dabrowski, and J. Przedmojski, *Liq. Cryst.*, **14**, 1377 (1993).
- [36] L. A. Karamysheva, K. V. Roitman, I. F. Agafonova, S. I. Torgova, R. Kh. Geivandov, V. F. Petrov, M. F. Grebyonkin, V. S. Bezborodov, N. P. Andryukhova, and N. A. Bumagin, *Mol. Cryst. Liq. Cryst.*, **191**, 259 (1990).
- [37] M. A. Mikhaleva, T. A. Kizner, N. I. Chernova, M. V. Loseva, G. A. Kolesnichenko, A. Z. Rabinovich, A. E. Juznetsova, and V. P. Mamaev, *Chem. Heterocycl. Comp.*, **25**, 1373 (1989).
- [38] H. Schubert, H.-J. Lorenz, R. Hoffman, and F. Franke, *Z. Chem.*, **6**, 337 (1966).
- [39] V. S. Bezborodov and V. F. Petrov, *Liq. Cryst.*, **23**, 771 (1997).
- [40] V. F. Petrov, *Liq. Cryst.*, **19**, 729 (1995).
- [41] V. F. Petrov, S. I. Torgova, L. A. Karamysheva, and S. Takenaka, *Liq. Cryst.*, **26**, 1141 (1999).
- [42] C. G. Le Fevre and R. J. W. Le Fevre, *J. Chem. Soc.*, 2750 (1955).
- [43] B. Schanker and J. Applequist, *J. Phys. Chem.*, **100**, 3879 (1996).
- [44] F. Mata, M. J. Quintana, and G. O. Sorensen, *J. Mol. Struct.*, **42**, 1 (1977).
- [45] G. O. Sorensen, L. Mahler, and N. Rastrup-Andersen, *J. Mol. Struct.*, **20**, 119 (1974).

- [46] H. C. Kjaergaard, R. J. Proos, D. M. Turnbull, and B. R. Hendry, *J. Phys. Chem.*, **100**, 19273 (1996).
- [47] M. A. Osman, *Z. Naturforsch.*, **38a**, 693 (1983).
- [48] M. A. Osman and L. Revesz, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 41 (1982).
- [49] B. I. Ostrovskii, *Structure and Bonding*, D. M. P. Mingos (ed.) (Springer, New York, 1999) p. 199.
- [50] W. Maier and G. Meier, *Z. Naturforsch. A*, **16**, 262 (1961).
- [51] M. Schadt, *Displays*, **13**, 11 (1992).
- [52] M. P. Bogaard, A. B. Buckingham, R. K. Pierens, and A. H. White, *J. Chem. Soc., Faraday Trans I*, **74**, 3008 (1978).
- [53] V. I. Minkin, O. A. Osipov, and Y. A. Zhdanov, *Dipole Moments in Organic Chemistry* (Plenum Press, New York, 1970).
- [54] W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials* (Gordon & Breach, New York, 1980).
- [55] W. H. de Jeu, C. J. Gerritsma, P. van Zanten, and W. A. Goosens, *Phys. Lett.*, **39A**, 355 (1972).
- [56] S. Ye. Yakovenko, A. A. Muravskii, F. Eikelschutle, and A. Geiger, *J. Chem. Phys.*, **105**, 10766 (1996).
- [57] I.-C. Khoo and S.-T. Wu, *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific Publishing, Singapore, 1993) Chap. 1.7.
- [58] E. Jakeman and E. P. Raynes, *Phys. Lett.*, **39A**, 69 (1972).