Lateral substitution in nematic systems

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Lateral substitution of mesogenic systems is shown to produce a great diversity of new liquid crystalline structures. The effect of such structural changes on the physico-chemical and electro-optical properties of laterally substituted nematic systems is discussed and compared with that of their unsubstituted analogues.

1. Introduction

Understanding the structure–property relations existing in liquid crystals continues to provide a considerable research challenge. It has been shown that even small structural changes of the molecules forming liquid crystals lead to the considerable changes of their physico-chemical and electro-optical properties [1–8]. One of the useful methods for the creation of new liquid crystalline (LC) structures with desirable characteristics is the lateral substitution of the molecular core by the alkyl, alkoxy, alkenyl, halogen, cyano, and other groups [1–3, 6–29]. The effect of lateral substitution on the physico-chemical and electro-optical properties of many nematic systems has been considered in past decades [1–3, 6–8, 13].

The present paper is not intended to be an updated comprehensive collection of laterally substituted nematic systems data. Rather, it will emphasize two major problems of the field. First, the structure–property relations existing in laterally substituted nematic systems will be critically discussed, underlining additional data explaining the experimental results. Second, a number of trends which seem to be emerging as basic principles of receiving laterally substituted liquid crystals with the desirable characteristics will be discussed, with the hope of raising additional research interest in this area.

2. Mesomorphic properties

The effect of lateral substitution on the mesomorphic properties of a compound has been found to be difficult

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to rationalize [1–3, 30–33]. It is therefore the purpose of this section to define what relations can be established for laterally substituted nematic systems, even though these may be empirical.

2.1. Lateral substitution of the 1,4-phenylene fragment
2.1.1. Effect of the type of laterial substituents on the mesomorphic properties

Among all known molecular fragments incorporated into the core of LC molecules, the 1,4-phenylene fragment is the most useful for lateral substitution [1–3, 6–8, 11–15, 18–20, 22–25, 27, 29]. Since most laterally substituted two-ring compounds are not mesomorphic or possess monotropic phase transitions [34–39], it would be better to consider the effects of lateral substitution of the 1,4-phenylene fragment incorporated into the molecular core of mostly three- and four-ring compounds.

The nature of lateral substituents has important implications on both the type of mesophase formed and phase transition temperatures. Among all known lateral substituents, the fluorine atom is the most useful owing to its small size leading to the least possible disruption of the lath-like nature of a laterally fluoro-substituted molecule with the simultaneous modification of its dipole moment [40, 41]. These features can be favourable for achieving desirable physico-chemical and electro-optical properties of liquid crystals and are illustrated by the following examples.

Tables 1–3 show the effect of the introduction of the different lateral substituents in the 1,4-phenylene fragment of the molecular core of liquid crystals on their mesomorphic properties (compounds **1-1**–**1-6**; **1-7**, **1-8**;

Table 1. Mesomorphic properties of liquid crystals:

$H_{11}C_5$—⟨⟩—⟨⟩—COO—⟨⟩—CN (I)
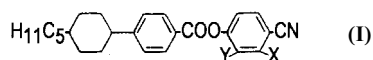
No.	X	Y	Phase transitions/°C	Reference
1-1	H	H	$Cr_2 82 Cr_1 111·5 N 226 I$	[52]
1-2	F	H	Cr90N195I	[22]
1-3	Cl	H	Cr88N147I	[22]
1-4	Br	H	Cr102N128I	[22]
1-5	CH_3	H	Cr83N135I	[22]
1-6	CN	H	Cr85·2N143·9I	[53]
1-7	H	F	Cr97N217I	[54]
1-8	H	CN	Cr132·2N178·7I	[53]

Table 2. Mesomorphic properties of liquid crystals:

H_9C_4—⟨⟩—COO—⟨⟩—⟨⟩—C_5H_{11} (II)

No.	X	Y	Phase transitions/°C	Reference
2-1	H	H	Cr123Sm136N184I	[9]
2-2	CH_3	H	Cr44N128I	[9]
2-3	OCH_3	H	Cr48Sm74N94I	[9]
2-4	C_2H_5	H	Cr47N67I	[9]
2-5	Cl	H	Cr54Sm110N129I	[9]
2-6	H	CH_3	Cr68N82I	[9]

2-1–2-5, 2-6; 3-1–3-3; 3-4, 3-5). As can be seen from these tables, lateral substitution of the 1,4-phenylene fragment incorporated into the molecular core of the given LC structures leads to a decrease in t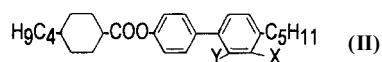he phase transition temperatures: crystal–nematic (smectic) [in some cases], smectic–nematic, and nematic–isotropic liquid in varying degrees depending on the type of lateral substituent.

It is useful to express the influence of the type of lateral substituents X on the mesomorphic properties of liquid crystals by the orders of increasing clearing temperature T_{cl} (nematic–isotropic liquid phase transition) and nematic range ΔT (see tables 1 and 2) shown overleaf. The results presented and data taken from the literature [1–3, 6–8, 18, 19, 42–58] reveal that lateral substitution of the 1,4-phenylene fragment of the molecular core of a liquid crystal by alkyl, alkoxy, alkenyl, halogen, NH_2, NO_2, CN groups have a considerable effect on their mesomorphic properties depending on the LC structure and type of lateral substituent and result in the reduction of the nematic thermostabilities, and in most cases, the smectic thermostabilities due to the lateral substituents broadening the molecule and reducing intermolecular forces.

On the one hand, it has been shown that increasing the length of a lateral alkyl chain correlated with its van der Waals volume results in a decrease in the clearing temperature of laterally substituted liquid crystals [9, 57, 58], and it has been proposed that there is a linear relationship between the phase transition temperatures and the van der Waals volume of lateral substituents X (F, CH_3, Cl, Br, NO_2, I) for laterally 3′-substituted 4′-n-alkoxybiphenyl-4-carboxylic acids with the following order of increasing clearing points [13]:

$$T_{cl} \rightarrow X: I < NO_2 < Br < Cl < CH_3 < F < H$$

On the other hand, the results received for the systems I and II make them difficult to follow that relationship [18, 47, 44].

The influence of the type of lateral substituent on the phase transition temperatures of laterally substituted liquid crystals can be explained using the results of X-ray diffraction investigations on the structure of the nematic phase. The investigation of polar liquid crystals by X-ray

Table 3. Physico-chemical properties of liquid crystals 3-1–3-5.

No.	Compound	Phase transitions/°C	d_1/Å	ξ_1/Å	d_2/Å	ξ_2/Å	Reference
3-1	H_7C_3—⟨⟩—⟨⟩—⟨N⟩—C_2H_5	Cr50·8Sm87·7N174·4I	19·5	46			[19, 62, 63]
3-2	H_7C_3—⟨⟩—⟨⟩(H_2N)—⟨N⟩—C_2H_5	S86N127I	21·7	110			[19, 62, 63]
3-3	H_7C_3—⟨⟩—⟨⟩(F)—⟨N⟩—C_2H_5	Cr60·2N145I	19·7	38			[19, 62, 63]
3-4	$H_{15}C_7$—⟨N⟩—⟨⟩—CN	Cr67N98·1I	20·2	33	29·3	60	[11, 14]
3-5	$H_{15}C_7$—⟨N HO⟩—⟨⟩—CN	Cr102N139·5			28·8	122	[11, 14]

H$_{11}$C$_5$⟨◯⟩—⟨◯⟩—COO—⟨◯⟩CN   **(I)** [22, 52, 53] Y=H, T_{cl} X: Br<CH$_3$<CN<Cl<F<H
                         Y   X

                                                        ΔT X: Br<CH$_3$<CN<Cl<F<H

H$_9$C$_4$⟨◯⟩—COO—⟨◯⟩—⟨◯⟩C$_5$H$_{11}$ **(II)** [9] Y=H, T_{cl} X: C$_2$H$_5$<OCH$_3$<CH$_3$<Cl<H
                         Y   X
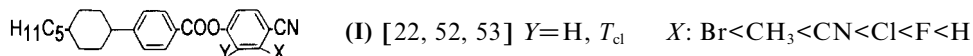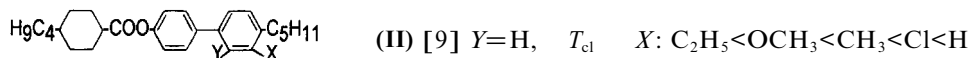
                                                        ΔT X: Cl<C$_2$H$_5$≈ OCH$_3$<H<CH$_3$

diffraction has revealed not only the existence of a layer structure in the smectic phase of these compounds but also periodic density fluctuations in the nematic phase having a period d [59–62]. They involve swarms containing tens to hundreds of molecules and are characterized by a correlation length ξ defined directly from the width of the diffraction peak. For the nematic phase of some two-ring cyano derivatives it has been shown that the ratio d/L, where L is a molecular length, is about 1·2–1·5 [59–62]. Hence the period of the fluctuating layer structure significantly exceeds a single molecular length, and should be related to the size of the molecular dimer. Such a dimer is formed by two polar molecules being mutually antiparallel. Experimental values of the layer structure of period d, for some other cyano derivatives showed that d depends on the molecular structure of the polar liquid crystals and characterizes in particular the degree of overlap of the molecular cores on dimer formation [59–62].

Further X-ray diffraction study of the nematic phase of polar liquid crystals revealed in some cases the simultaneous existence of two fluctuation layer structures with incommensurate periods d_1 and d_2, where $d_1 < L$ and $L < d_2 < 2L$ [60–62].

For weakly polar compounds **3-1**–**3-3** (see table 3) only the monomeric density wave was observed with a characteristic period d_1 [19, 62, 63]. A somewhat unusual situation has been observed for compound **3-2**. The length of its molecular agrees with that for **3-1** and **3-3**, but d_1 is appreciably greater. Presumably, due to the interaction with a neighbouring molecule (taking into account the attraction and steric factors), the presence of the lateral substituent NH$_2$ leads to a fluctuation layered structure whose period is greater than the length of an individual molecular as a result of a longitudinal shift of neighbouring molecules relative to one another. Compound **3-2** having the highest value of the correlation length ξ_1 can be considered the most smectogenic (potentially) and compound **3-3** with a fluorine atom as a lateral substituent is the least smectogenic among the compounds **3-1**–**3-3** [62, 63].

It has been shown that the lateral hydroxy substitution of the 1,4-phenylene fragment of 5,6,7,8-tetrahydro-

quinoline cyano derivatives results in increasing the melting and clearing points compared to those of the corresponding unsubstituted analogues (compounds **3-4** and **3-5**, table 3) [11, 14]. This may well be due to the enhanced axial molecular polarizability resulting from delocalization of π-electrons caused by intramolecular hydrogen bonding, which is possibly responsible for the disappearance of the local smectic-like fluctuations of the monomeric density wave observed from the X-ray diffraction study of the structure of the nematic phase [14]. Similar effects caused by intramolecular hydrogen bonding have been found for other laterally hydroxy substituted derivatives [11].

2.1.2. *Influence of the position of lateral substituent in the 1,4-phenylene fragment on the mesomorphic properties*

The data collated in tables 1, 2 and 4 reveal that the position of the lateral substituent in the 1,4-phenylene fragment incorporated into the molecular core of the liquid crystals has a considerable effect on their mesomorphic properties (compounds **1-1**, **1-2** and **1-7**, **1-6** and **1-8**; **2-1**, **2-2** and **2-6**; **4-1**, **4-2** and **4-3**).

The introduction of a fluoro substituent in the *ortho* or *para* positions to the terminal cyano group of system (**I**) effectively reduces both the clearing and melting points compared to those of the parent compound (compounds **1-1**, **1-2** and **1-7**, table 1). This reduction of the phase transition temperatures is more pronounced for *ortho* substitution. In the case of lateral cyano substitution, again laterally *ortho* substituted liquid crystals exhibit lower values of melting and clearing temperatures (compounds **1-1**, **1-6** and **1-8**, table 1). Interestingly, *para* substitution of the cyano group in system (**I**) even leads to a higher melting point compared with its unsubstituted analogue (compounds **1-1** and **1-8**).

Both lateral methyl substitutions in the *ortho* or *para* positions to the terminal pentyl group of system (**II**) produce liquid crystals exhibiting only the nematic phase with lower values of crystal–nematic and nematic–isotropic liquid phase transition temperatures (compounds **2-2** and **2-6**, table 2), and a broader nematic range (compound **2-2**) than the corresponding parent compound

2-1. In this case, the reduction of the clearing and melting points is more pronounced for compounds having lateral *para* and *ortho* methyl substituents, respectively.

The phase transition temperatures for compounds **4-1**, **4-2**, **4-3** (see table 4) show how strongly the smectic character of the parent compound **4-1** is reduced (compound **4-2**) or removed with increasing the nematic range (compound **4-3**) by lateral fluoro substitution. The clearing temperatures for compounds **4-2** and **4-3** are very similar and the lower smectic character of compound **4-3** is associated with the C–F bond pointing towards the nitrogen atom of the pyridin-2,5-diyl fragment [65].

The influence of the position of the lateral fluoro substituent in the 1,4-phenylene fragment incorporated into the molecular core of the liquid crystalline systems on their mesomorphic properties can be expressed by orders of increasing clearing points and nematic ranges depending on the lateral substituents X and Y introduced into the 1,4-phenylene fragment (see tables 1, 2 and 4), as shown below.

These results show that the position of a lateral substituent in the 1,4-phenylene fragment has a strong influence on the mesomorphic properties of a given system leading in most cases to the reduction of the nematic and smectic thermostabilities [1–3, 6–8, 34, 35, 42, 43, 66–104].

Higher values of clearing points observed for some 2-fluoro substituted cyano derivatives compared to those of their unsubstituted analogues were explained in terms of molecular association [2, 54, 67, 71–77, 96–99].
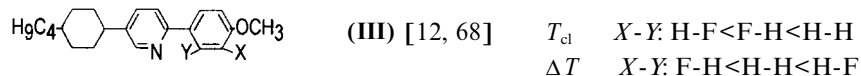

(I) [22, 52-54]　　T_{cl}　　X-Y: F-H<H-F<H-H

　　　　　　　　　　　ΔT　　X-Y: F-H<H-H<H-F

(II) [9]　　T_{cl}　　X-Y: H-CH$_3$<CH$_3$-H<H-H

　　　　　　　ΔT　　X-Y: H-CH$_3$<H-H<CH$_3$-H

(III) [12, 68]　　T_{cl}　　X-Y: H-F<F-H<H-H

　　　　　　　　　　ΔT　　X-Y: F-H<H-H<H-F
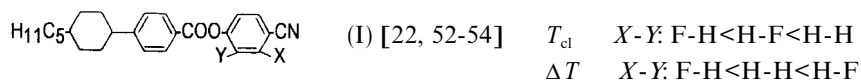
Table 4.　Mesomorphic properties of liquid crystals **4-1**–**4-9**.

No.	Compound	Phase transitions/°C	Reference
4-1		Cr87Sm142N208I	[64]
4-2		Cr94Sm138·8N179·8I	[64]
4-3		Cr45·2N174·5I	[12]
4-4		Cr109N237·5I	[50]
4-5		Cr98N146I	[22]
4-6		Cr86I	[25]
4-7		Cr82N121I	[128]
4-8		Cr74·8N95·9I	[35]
4-9		Cr14·7N47I	[26]

Table 5. Mesomorphic properties of liquid crystals:

$$H_{11}C_5 \left\langle \begin{array}{c} O \\ B \\ O \end{array} \right\rangle \!\!-\!\!\left\langle \right\rangle\!\!-\!\!COO\!\!-\!\!\left\langle \right\rangle\!\!-\!\!Z \quad \text{(IV)}$$
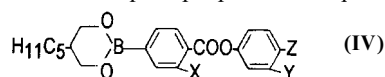
No.	X	Y	Z	Phase transitions/°C	Reference
5-1	H	H	CN	Cr127N192I	[24]
5-2	F	H	CN	Cr94N167I	[23]
5-3	F	F	CN	Cr63N142I	[23]
5-4	H	Cl	CN	Cr106N117I	[23]
5-5	Cl	H	CN	Cr93N109I	[23]
5-6	Cl	Cl	CN	Cr86I	[23]
5-7	Cl	F	CN	Cr59N74I	[23]
5-8	F	Cl	CN	Cr105I	[23]
5-9	H	H	NCS	Cr131·1SmA145·7N188I	[29]
5-10	H	F	NCS	$Cr_1$51Cr115·8SmA151·1N178I	[29]
5-11	F	H	NCS	Cr104N163·5I	[29]
5-12	F	F	NCS	Cr49·4SmA110·7N155·4I	[29]
5-13	H	H	F	$Cr_2$65·7$Cr_1$70·4Cr75·3SmA80·6N118I	[29]
5-14	H	F	F	Cr69·2SmA85N99·2I	[29]
5-15	F	H	F	$Cr_1$55·5Cr61·6N80·3I	[29]
5-16	F	F	F	Cr50·1Sm(44·5)N70·5I	[29]
5-17	H	H	OCF_3	Cr68·9SmA138·1I	[29]
5-18	F	H	OCF_3	Cr48·4SmA111N113·9I	[29]
5-19	H	H	CF_3	$Cr_2$71·5$Cr_1$75Cr89·5SmA135·2I	[29]
5-20	F	H	CF_3	Cr74·4SmA102·8I	[29]

2.1.3. *Influence of the quantity of lateral substituents and their positions in the molecular core of liquid crystals on their mesomorphic properties*

As mentioned above, the position of the lateral substituent in the 1,4-phenylene fragment of the molecular core of liquid crystals has a significant influence on their mesomorphic properties. Similar effects have been found for compounds having a laterally substituted 1,4-phenylene fragment in different positions in their cores.

The data collated in table 5 show that both lateral 3-chloro and 3′-chloro substitutions of cyano derivatives of system (**IV**) result in decreasing melting and clearing temperatures compared to those of the parent compound (compounds **5-1**, **5-4** and **5-5**), while the decrease in the phase transition temperatures is more pronounced for the latter having the lateral 3′-chloro substituent. In the case of lateral fluoro substitutions of propyl, butyl, pentyl, hexyl and heptyl homologues of cyano derivatives (see systems **IV** and **V**, tables 5 and 6), again, the reduction of the clearing points was observed (compounds **5-1** and **5-2**; **6-1**, **6-2**, **6-3**; **6-5**, **6-6**, **6-7**; **6-9**, **6-10**; **6-12**, **6-13**), while the reduction of the melting points was found for almost all these compounds under consideration, except compound **6-3**. As can be seen from table 6, laterally 3-fluoro or 3′-fluoro substituted propyl homologues of the cyano derivatives of system **V** (compounds **6-2** and **6-3**) have almost the same clearing temperatures and differ in the melting points with the higher value belonging to the latter having a 3-fluoro-

Table 6. Mesomorphic properties of liquid crystals:

$$H_{2n+1}C_n \left\langle \begin{array}{c} O \\ B \\ O \end{array} \right\rangle \!\!-\!\!\left\langle \right\rangle\!\!-\!\!COO\!\!-\!\!\left\langle \right\rangle\!\!-\!\!CN \quad \text{(V)}$$
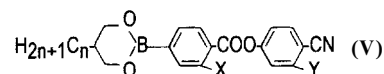
No.	n	X	Y	Phase transitions/°C	Reference
6-1	3	H	H	Cr105N201I	[24]
6-2	3	F	H	Cr89N174I	[23]
6-3	3	H	F	Cr126N173·5I	[23]
6-4	3	F	F	Cr103N143·5I	[23]
6-5	4	H	H	Cr121N197I	[24]
6-6	4	F	H	Cr95N168I	[23]
6-7	4	H	F	Cr103N164I	[23]
6-8	4	F	F	Cr64N143I	[23]
6-9	6	H	H	Cr123N182I	[24]
6-10	6	F	H	Cr97N157I	[23]
6-11	6	F	F	Cr68N131I	[23]
6-12	7	H	H	Cr108N181I	[24]
6-13	7	F	H	Cr95N153I	[23]
6-14	7	F	F	Cr71N131I	[23]

4-phenyl fragment. For the butyl homologues the same tendency in the phase transition temperatures was observed with a more pronounced difference in the clearing points (compounds **6-6** and **6-7**).

The replacement of the terminal cyano group by the NCS group in compound **5-1** to produce compound **5-9** results in slightly increasing the melting point, decreasing the clearing point and the appearance of the smectic A phase with high thermostability (see table 5). Both

Table 7. Mesomorphic properties of liquid crystals:

H_7C_3—⟨ ⟩—⟨ ⟩—⟨ ⟩^Z_X (VI)
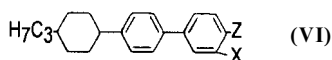
No.	X	Z	Phase transitions/°C	Reference
7-1	H	OCF_2Cl	Cr96Sm112·5N123I	[27]
7-2	F	OCF_2Cl	Cr43N75I	[27]
7-3	H	$OCHF_2$	Cr82Sm121·1N169·4I	[20]
7-4	F	$OCHF_2$	Cr50·5N118·4I	[20]
7-5	H	OCF_2CHFCF_3	Cr118·2SmB176·4N181·9I	[125]
7-6	F	OCF_2CHFCF_3	Cr50·7SmB97·5SmA124·1N148·1I	[125]
7-7	H	Cl	Cr158N189I	[121]
7-8	F	Cl	Cr108N143·5I	[119]
7-9	H	OCH_2CF_3	Cr100SmB170SmA194I	[122]
7-10	F	OCH_2CF_3	Cr81SmB101SmA133N139·6I	[122]
7-11	H	F	Cr98·3N153·4I	[149]
7-12	F	F	Cr67·9N98·6I	[35]

lateral 3-fluoro or 3′-fluoro substitutions of compound **5-9** decreases its clearing and melting points, while the smectic A phase disappears with increasing nematic range in the latter case and exhibits increased thermostability in the former case (compounds **5-10**, **5-11**).
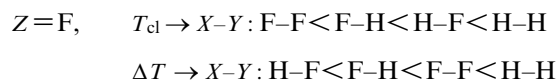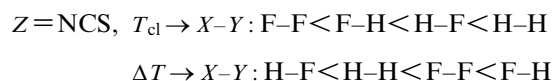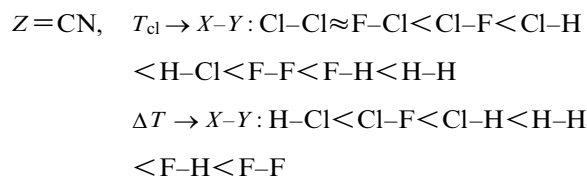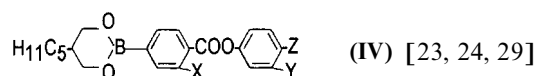
Similar tendencies in the phase transition temperatures were found for the terminally fluoro-substituted derivative of system **IV** and its laterally fluoro-substituted analogues (compounds **5-13**–**5-15**, table 5). Increasing the number of lateral substituents in the molecular core of liquid crystals further lowers the melting and clearing points with a more pronounced effect found for chloro substituents (compounds **5-1**, **5-3**, **5-6**) and can increase the nematic range (compounds **5-1** and **5-3**; **6-5** and **6-8**; **6-9** and **6-11**; tables 5 and 6). The introduction of the different lateral substituents (fluoro and chloro) in the same molecular core of the liquid crystals also leads to a decrease in the melting and clearing points compared to those of the parent compounds (compounds **4-7**, **4-8** and **4-9**; **5-1**, **5-7**, **5-8**; tables 4 and 5) with a more pronounced effect being found for compound **5-8** having 3′-fluorophenyl and 3-chlorophenyl fragments.

Table 8. Mesomorphic properties of liquid crystals:

$H_{2n+1}C_n$—⟨ ⟩^O_OB—⟨ ⟩$^{COOH}_X$ (VII)
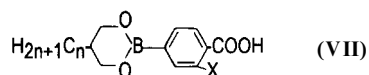
No.	n	X	Phase transitions/°C	Reference
8-1	4	H	Cr221I	[24]
8-2	4	F	Cr164N169I	[23]
8-3	5	H	Cr198N208I	[24]
8-4	5	F	Cr156N174I	[23]
8-5	6	H	Cr153N193I	[24]
8-6	6	F	Cr158N167I	[23]
8-7	7	H	Cr165N202I	[24]
8-8	7	F	Cr147N169I	[23]

The efficiency of the lateral substituents and their positions in the molecular core of the liquid crystals of system **IV** can be derived as follows (see table 5):

$H_{11}C_5$—⟨ ⟩^O_OB—⟨ ⟩$^{COO}_X$—⟨ ⟩^Z_Y (IV) [23, 24, 29]

$Z = CN$, $T_{cl} \to X$–Y : Cl–Cl$\approx$F–Cl$<$Cl–F$<$Cl–H

$<$H–Cl$<$F–F$<$F–H$<$H–H

$\Delta T \to X$–Y : H–Cl$<$Cl–F$<$Cl–H$<$H–H

$<$F–H$<$F–F

$Z = NCS$, $T_{cl} \to X$–Y : F–F$<$F–H$<$H–F$<$H–H

$\Delta T \to X$–Y : H–F$<$H–H$<$F–F$<$F–H

$Z = F$, $T_{cl} \to X$–Y : F–F$<$F–H$<$H–F$<$H–H

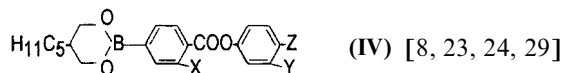$\Delta T \to X$–Y : H–F$<$F–H$<$F–F$<$H–H

These results and the data on the phase transition temperatures presented in tables 5 and 6 clearly show that the lateral mono and double fluoro substitution of the cyano and isothiocyanato derivatives of systems **IV** and **V** produce low melting liquid crystals with broad nematic ranges which can be used as the components of wide temperature range liquid crystalline materials for display applications [15].

It has been shown that increasing the number of lateral substituents introduced in the 1,4-phenylene fragment incorporated into the molecular core of liquid crystals further decreases the clearing points leading in some cases to the disappearance of the nematic phase (compounds **4-4**–**4-6**, table 4). Similar effects have been found for other liquid crystalline derivatives [22–24, 26, 34, 35, 40, 43, 46, 50, 66, 80, 83, 85–87, 94, 105–118].

2.1.4. *Influence of lateral substitution on the terminal group's efficiency*

It has been found that lateral substitution of the 1,4-phenylene fragment incorporated into the molecular core of liquid crystals may affect the terminal group's efficiency by different degrees (see tables 5 and 7) [8, 23, 24, 29]:

$$H_{11}C_5 \overset{O}{\underset{O}{\diamond}}B \text{—} \underset{X}{\bigcirc} \text{COO} \underset{Y}{\bigcirc} Z \qquad \textbf{(IV)} \; [8, 23, 24, 29]$$

$X = H, Y = H, \; T_{cl} \to Z: F < CF_3 < OCF_3 < NCS < CN$

$\Delta T \to Z: F < NCS < CN$

$T_{SmA} \to Z: F < CF_3 < OCF_3 < NCS$

$\Delta T_{SmA} \to F < NCS < CF_3 < OCF_3$

$X = F, Y = H, \; T_{cl} \to Z: F < CF_3 < OCF_3 < NCS < CN$

$\Delta T \to Z: F < NCS < CN$

$T_{SmA} \to Z: CF_3 < OCF_3$

$\Delta T_{SmA} \to CF_3 < OCF_3$

$X = F, Y = F, \; T_{cl} \to Z: F < CN < NCS$

$\Delta T \to Z: F < NCS < CN,$

where T_{SmA} and ΔT_{SmA} are the thermostability and range of the smectic A phase, respectively.

Similar relationships can be derived for other liquid crystalline derivatives:

$$H_7C_3 \bigcirc \text{—} \bigcirc \text{—} \underset{X}{\bigcirc} Z \qquad \textbf{(VI)} \; [20, 27, 124\text{-}127]$$
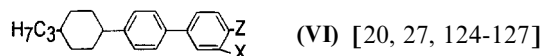
$X = H, \; T_{cl} \to Z: OCF_2Cl < F < OCHF_2$

$< OCF_2CHFCF_3 < Cl < OCH_2CF_3$

$\Delta T \to Z: OCH_2CF_3 < OCF_2CHFCF_3$

$< OCF_2Cl < Cl < OCHF_2 < F$

$X = F, \; T_{cl} \to Z: OCF_2Cl < F < OCHF_2 < OCH2CF_3$

$< Cl < OCF_2CHFCF_3$

$\Delta T \to Z: OCH_2CF_3 < OCF_2CHFCF_3 < F$

$< OCF_2Cl < Cl < OCHF_2.$

As can be seen from these results and data taken from the literature, lateral substitutions of the 1,4-phenylene fragment of the molecular core of liquid crystals can affect the efficiency of the attached terminal groups depending on the molecular structure of the liquid crystal, position and type of lateral substituent. So far, increasing the number of saturated molecular fragments, such as a *trans*-1,4-cyclohexylene fragment, results in the lower alteration of the orders of increasing T_{cl} and ΔT of nematic systems caused by their lateral substitution, while increasing the number of lateral substituents and 1,4-phenylene fragments in the core gives a more pronounced effect on the T_{cl} and ΔT orderings [20, 23, 24, 27, 29, 34, 39–41, 47, 48, 51–53, 83, 89, 90, 94, 95, 100, 109, 110, 112, 113, 119–135].

The odd–even effect is well known and observed for many homologous series of liquid crystals, especially for two-ring compounds [3, 7, 19, 136]. This can be explained by the odd carbon atom alkyl chain having a terminal CH_3 group which extends the long molecular axis, whereas in an even number carbon chain the terminal CH_3 group tends to lie off axis [7]. In the corresponding alkoxy substituted series, the oxygen is equivalent to a CH_2 group and the reverse situation is found [136].

One can expect that the lateral substitution of the 1,4-phenylene fragment incorporated into the molecular core of liquid crystals may affect their alkyl chain's efficiency, particularly the odd–even effect. The proposed influence is not found for the compounds presented in tables 5 and 6 (see system **V**). However, systems **VII** (see table 8) and **VIII** (see table 9) show that the lateral substitution may affect the terminal alkyl group's efficiency in different degrees depending on the molecular structure of the liquid crystal and the position and type of the lateral substituents.

$$H_{2n+1}C_n \overset{O}{\underset{O}{\diamond}}B \text{—} \underset{X}{\bigcirc} \text{COO} \underset{Y}{\bigcirc} CN \qquad \textbf{(V)} \; [23, 29]$$
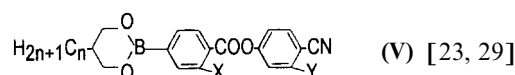
$X = H, Y = H \; T_{cl} \to n: n=7 < n=6 < n=5 < n=4 < n=3$

$\Delta T \to n: n=6 < n=5 < n=7 < n=4 < n=3$

$X = F, Y = H \; T_{cl} \to n: n=7 < n=6 < n=5 < n=4 < n=3$

$\Delta T \to n: n=7 < n=6 < n=5 \approx n=4 < n=3$

$X = H, Y = F \; T_{cl} \to n: n=5 < n=4 < n=3$

$\Delta T \to n: n=5 < n=3 < n=4$

$X = F, Y = F \; T_{cl} \to n: n=7 < n=6 < n=5 < n=4 < n=3$

$\Delta T \to n: n=3 < n=7 < n=6 < n=5 < n=4$

$$H_{2n+1}C_n \overset{O}{\underset{O}{\diamond}}B \text{—} \underset{X}{\bigcirc} \text{COOH} \qquad \textbf{(VII)} \; [23, 24]$$
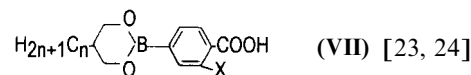
$X = H, \; T_{cl} \to n: n=4 < n=6 < n=7 < n=5$

$\Delta T \to n: n=5 < n=7 < n=6$

$X = F, \; T_{cl} \to n: n=6 < n=7 \approx n=4 < n=5$

$\Delta T \to n: n=4 < n=6 < n=5 < n=7$

(VIII) [19]
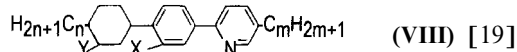
$X = $ H, $Y = $ H, $\quad T_{cl} \rightarrow n\text{-}m$: 2-5 < 2-3 < 5-2 < 3-2

< 3-5 < 5-3

$\Delta T \rightarrow n\text{-}m$: 2-3 < 2-5 < 3-5 < 5-3

< 3-2 < 5-2

$X = $ NH$_2$, $Y = $ H, $\quad T_{cl} \rightarrow n\text{-}m$: 2-3 < 2-5 < 3-2 < 5-2

< 3-5 < 5-3

$\Delta T \rightarrow n\text{-}m$: 5-3 < 2-3 < 3-2 < 3-5

< 5-2 < 2-5

$X = $ F, $Y = $ H, $\quad T_{cl} \rightarrow n\text{-}m$: 2-5 < 2-3 < 5-2 < 3-5

< 3-2 < 5-3

$\Delta T \rightarrow n\text{-}m$: 2-3 ≈ 2-5 < 5-2 < 3-2

≈ 5-3 < 3-5.

Similar results have been found for other liquid crystalline derivatives [22, 34, 35, 48, 52, 70, 71, 75, 79, 82, 88–90, 96, 104, 128–148].

2.1.5. *Influence of lateral substitution on the molecular core's efficiency*

It has been found that lateral substitution of the 1,4-phenylene fragment incorporated into a LC molecular core can affect its efficiency depending on the LC molecular structure, type and position of the lateral substituent [8]. This is illustrated by the following orders of increasing the clearing points and nematic ranges depending on the type of molecular fragment A (see tables 1 and 5, [8, 22, 78]):

(IX) [8, 22]
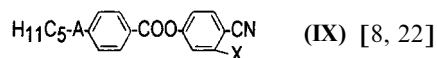
$X = $ H, $\quad T_{cl} \rightarrow A$: BDox < Ch < Ph < Dox

$\Delta T \rightarrow A$: BDox < Dox < Ch < Ph

$X = $ Cl, $\quad T_{cl}\Delta T \rightarrow A$: BDox < Dox < Ph < Ch

$X = $ F, $\quad T_{cl} \rightarrow A$: BDox < Ph < Ch

$\Delta T \rightarrow A$: BDox < Ch < Ph
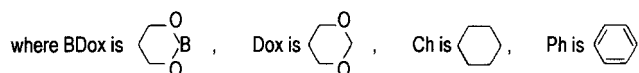
Similar relationships have been found for other liquid crystalline derivatives [8]. The results presented reveal the strong dependence of the mesomorphic properties of laterally substituted 1,4-phenylene derivatives on their molecular structure, quantity, type and position of the lateral substituents.

2.2. *Lateral substitution of the* trans-*1,4-cyclohexylene fragment*

Bearing in mind the fascinating variations in LC physical properties that may be brought about in nematic systems having a laterally substituted 1,4-phenylene fragment and related directly to molecular structural changes, it would be satisfying to make such comparisons for liquid crystalline systems containing a laterally substituted *trans*-1,4-cyclohexylene fragment and be able to tune their properties to display applications.

It has been found that the introduction of fluorine and oxygen atoms, and methyl and cyano groups in the *trans*-1,4-cyclohexylene fragment belonging to the molecular core of liquid crystalline derivatives sufficiently reduces their nematic thermostabilites, and in most cases, smectic thermostabilities; and for two-ring compounds, can lead to monotropic phase transitions or even to the disappearance of the mesophase due to the lateral substituents broadening the molecule and reducing intermolecular forces [10, 11, 17, 18, 25, 28, 150–153]. These effects are more pronounced for three- and four-ring liquid crystals and can be illustrated by comparing the phase transition temperatures of the liquid crystals presented in tables 9–11.

The introduction of a methyl group or fluorine atoms in the lateral positions of the *trans*-1,4-cyclohexylene fragment incorporated into the molecular core of liquid crystals of given structures results in decreasing the clearing points compared to those of the parent compounds (compounds **3-1** and **9-7**; **9-8** and **9-11**; **9-12** and **9-15**; **9-16** and **9-19**; **10-1** and **10-2**; **10-1** and **10-4**; **10-5**, **10-7** and **10-8**; tables 9 and 10). The smectic thermostability of laterally methyl substituted liquid crystals can be increased (compounds **10-7** and **10-8**) and decreased (compounds **3-1** and **9-7**; **9-8** and **9-11**; **9-12** and **9-15**; **9-16** and **9-19**) in comparison with the parent compounds. It has been found that laterally fluoro-substituted liquid crystals exhibit smectic thermostability with lower values compared to those of their laterally unsubstituted analogue (compounds **10-3** and **10-4**, **10-5**). The melting points exhibit both the increase (compounds **3-1** and **9-7**; **10-1** and **10-2**; **10-3** and

Table 9. Mesomorphic properties of liquid crystals:

(VIII)
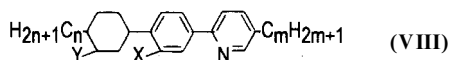
| No.	n	m	X	Y	Phase transitions/°C	Reference
9-1	2	3	H	H	Cr51·9Sm92·7N158·8I	[19]
9-2	2	3	NH$_2$	H	Sm69N105I	[19]
9-3	2	3	F	H	Cr47·6N127·5I	[19]
9-4	2	5	H	H	Cr40·2Sm84·6N153·1I	[19]
9-5	2	5	NH$_2$	H	Sm60N113I	[19]
9-6	2	5	F	H	Cr39·5N119·5I	[19]
3-1	3	2	H	H	Cr50·8Sm87·7N174·4I	[19]
3-2	3	2	NH$_2$	H	Sm86N127I	[19]
3-3	3	2	F	H	Cr60·2N145·1I	[19]
9-7	3	2	H	CH$_3$	Cr62N95·6I	[11]
9-8	3	5	H	H	Cr48Sm93·8N177·4I	[19]
9-9	3	5	NH$_2$	H	Sm102N146I	[19]
9-10	3	5	F	H	Cr52·9N144·6I	[19]
9-11	3	5	H	CH$_3$	Cr47Sm50·6N111·1I	[11]
9-12	5	2	H	H	Cr65·8Sm78N168I	[19]
9-13	5	2	NH$_2$	H	Sm80N128I	[19]
9-14	5	2	F	H	Cr60N142I	[19]
9-15	5	2	H	CH$_3$	Cr34N94·7I	[11]
9-16	5	3	H	H	Cr37Sm93·5N179I	[19]
9-17	5	3	NH$_2$	H	Sm116N147I	[19]
9-18	5	3	F	H	Cr66N151I	[19]
9-19	5	3	H	CH$_3$	Cr15N111I	[11]

Table 11. Mesomorphic properties in liquid crystals:

(XII)
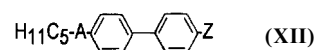
No.	A†	Z	Phase transitions/°C	Reference
11-1	Ch	H	Cr58Sm81N98I	[47]
11-2	ChO	H	Cr75SmA96I	[154]
11-3	Ch	CH$_3$	Cr98Sm123N178I	[47]
11-4	ChO	CH$_3$	Cr84SmA148N152I	[154]
11-5	Ch	OCH$_3$	Cr80N165I	[83]
11-6	ChO	OCH$_3$	Cr112N178I	[154]
11-7	Ch	F	Cr100N153I	[83]
11-8	ChO	F	Cr74N126I	[28]

† Ch is , ChO is
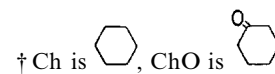
10-4, 10-5) and decrease (compounds 9-8 and 9-11; 9-12 and 9-15; 9-16 and 9-19; 10-7 and 10-8) for laterally methyl of fluoro-substituted liquid crystals. Interestingly, increasing the quantity of lateral fluorine atoms introduced in the *trans*-1,4-cyclohexylene fragment leads to increasing the melting points, decreasing the smectic (T_{Sm}) and nematic thermostabilities (compounds 10-3–10-5, table 10):

Table 10. Mesomorphic properties of liquid crystals 10-1–10-10.

No.	Compound	Phase transitions/°C	Reference
10-1		Cr96N222I	[83]
10-2		Cr97N158I	[10]
10-3		Cr41Sm156N160I	[124]
10-4		Cr45Sm135N140I	[17]
10-5		Cr78SmA90N99I	[28]
10-6		Cr99SmB142·5N152I	[154]
10-7		Cr85·2N240·8I	[95]
10-8		Cr66Sm77N196I	[25]
10-9		Cr93N147I	[25]
10-10		Cr50N68I	[18]

(X) [18, 28, 124]
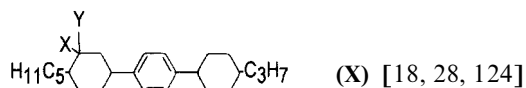
$$T_{cl} \rightarrow X-Y : F-F < F-H < H-H$$

$$\Delta T \rightarrow X-Y : H-H < F-H < F-F$$

$$T_{Sm} \rightarrow X-Y : F-F < F-H < H-H$$

$$\Delta T_{Sm} \rightarrow X-Y : F-H < F-F < H-H,$$

where ΔT_{Sm} is the smectic range.

As supported by the data presented in tables 10 and 11, the oxidation of the *trans*-1,4-cyclohexylene fragment of the molecular core of given liquid crystals results in decreasing the clearing points (compounds **10-3** and **10-6**; **11-1** and **11-2**; **11-3** and **11-14**; **11-7** and **11-8**) for weakly polar alkyl, dialkyl and polar derivatives; increasing the clearing points (compounds **11-5** and **11-6**) for alkyl–alkoxy derivatives compared with those of the corresponding parent compounds. The melting temperatures and smectic thermostabilities of the compounds presented exhibit a more complicated character: increase (compounds **10-3** and **10-6**; **11-1** and **11-12**; **11-5** and **11-6**) and decrease (compounds **11-3** and **11-4**; **11-7** and **11-8**) of the melting points; increase (compounds **11-1** and **11-2**; **11-3** and **11-4**) and decrease (compounds **10-3** and **10-6**) of the smectic thermostability, respectively.

The influence of the quantity of lateral substituents in the *trans*-1,4-cyclohexylene fragment belonging to molecular core of liquid crystals on their mesomorphic properties can be expressed by the following orders of increasing clearing points and nematic ranges (compounds **10-7**–**10-9**, table 10), as shown below. As can be seen for the system **XI**, increasing the quantity of lateral substituents introduced in the *trans*-1,4-cyclo-hexylene fragment of the LC molecular core results in decreasing the clearing temperatures of liquid crystals. The same results were obtained for liquid crystals having a laterally multi-substituted 1,4-phenylene fragment (see §2.1.3).

As can be seen from tables 2 and 10, the introduction of a methyl group in the lateral position of the *trans*-1,4-cyclohexylene fragment of the molecular core of laterally chloro-substituted liquid crystalline compound **2-5** to produce compound **10-10** further reduces the clearing and melting points compared to those of the laterally unsubstituted analogue **2-1** and creates only the nematic phase.
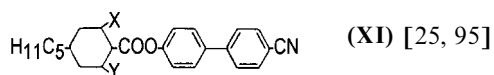
The data collated in table 11 show that the oxidation of the *trans*-1,4-cyclohexylene fragment of system **XII** affects the ordering of the nematic ranges and has no influence on the ordering of the clearing points in dependence on the terminal groups Z:

(XII) [28, 47, 83, 154]

$$A = Ch, \quad T_{cl} \rightarrow Z : H < F < OCH_3 < CH_3$$
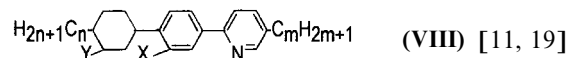
$$\Delta T \rightarrow Z : H < F < CH_3 < OCH_3$$

$$A = ChO, \quad T_{cl} \rightarrow Z : H < F < CH_3 < OCH_3$$

$$\Delta T \rightarrow Z : CH_3 < F < OCH_3,$$

where ChO is

As in the case of the 1,4-phenylene fragment, lateral substitution of the *trans*-1,4-cyclohexylene fragment belonging to the molecular core of liquid crystals can affect the terminal group's efficiency (see table 9):

(VIII) [11, 19]

$$X = H, \; Y = H, \quad T_{cl} \rightarrow n\text{-}m : 5\text{-}2 < 3\text{-}2 < 3\text{-}5 < 5\text{-}3$$

$$\Delta T \rightarrow n\text{-}m : 3\text{-}5 < 5\text{-}3 < 3\text{-}2 < 5\text{-}2$$

$$X = H, \; Y = CH_3, \; T_{cl} \rightarrow n\text{-}m : 5\text{-}2 < 3\text{-}2 < 5\text{-}3 \approx 3\text{-}5$$

$$\Delta T \rightarrow n\text{-}m : 3\text{-}2 < 3\text{-}5 < \approx 5\text{-}2 < 5\text{-}3$$

The results presented reveal the strong dependence of the mesomorphic properties of laterally substituted *trans*-1,4-cyclohexylene derivatives on their molecular structure, quantity, type, and position of the lateral substituents.

2.3. *Lateral substitution of the 1,4-cyclohexenylene fragment*

The data presented in table 12 show the phase transition temperatures of laterally substituted 1,4-cyclo-hexenylene derivatives and their unsubstituted analogues. The introduction of the lateral cyano, chloro and methyl groups in the 1,4-cyclohexenylene fragment of the compounds **12-1** and **12-3** to produce the compounds **12-2** and **12-4**, **12-5**, respectively, effectively reduces the melting points leading to the disappearance of the nematic phase; while lateral double methyl substitution of the


(XI) [25, 95] T_{cl} $X\text{-}Y$: $CH_3\text{-}CH_3 < CH_3\text{-}H < H\text{-}H$

           ΔT $X\text{-}Y$: $CH_3\text{-}CH_3 < CH_3\text{-}H < H\text{-}H$

Table 12. Mesomorphic properties of liquid crystals **12-1**–**12-9**.

| No.	Compound, $R = C_5H_{11}$	Phase transitions/°C	Reference
12-1	R—Ph—Ph—Ph—F	Cr68N107I	[155]
12-2	H₃C lateral, R—Ph—Ph—Ph—F	Cr58I	[155]
12-3	R—Ph—Ceh—Ph—C₃H₇	Cr83N113·6I	[155]
12-4	Cl lateral, R—Ph—Ceh—Ph—C₃H₇	Cr40·6I	[155]
12-5	NC lateral, R—Ph—Ceh—Ph—C₃H₇	Cr50·5I	[155]
12-6	R—Ch—COO—Ph—Ph—CN	Cr64N165I	[25]
12-7	CH₃, CH₃ lateral, R—Ch—COO—Ph—Ph—CN	Cr69N103I	[25]
12-8	R—Ch—Ph—OC₂H₅	Cr79N(76)I	[28]
12-9	O= R—Ceh—Ph—OC₂H₅	Cr70SmA86I	[156]

compound **12-6** produces the liquid crystal **12-7** with sufficiently decreased clearing point and slightly increased melting point.

As can be seen from table 12, replacement of the 1,4-cyclohexenylene fragment by the 3,6-cyclohex-2-en-1-one fragment in compound **12-8** to produce compound **12-9** results in the disappearance of the monotropic nematic phase, decreasing the melting point and promoting the appearance of the smectic A phase with a high thermostability.

The efficiency of the molecular fragments *A* belonging to the molecular core of system **XII** can be derived as follows:

H₁₁C₅-A—Ph—OC₂H₅   **(XIII)** [20, 28, 154, 156-158]

T_{cl} *A*: ⟨structures⟩
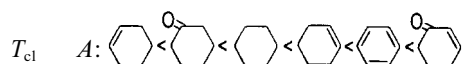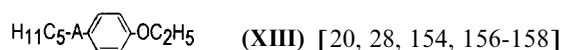
Similar relationships have been found showing the efficiency of the molecular fragments incorporated into the molecular core of systems **XIV**–**XVI** [156], as shown overleaf. It has been found that the influence of lateral methyl substitution on the efficiency of molecular fragments of system **XVII** can be expressed by the orders of increasing T_{cl} and ΔT [9] shown overleaf.

where Ph is ⬡, Ch is ⬡   Ceh is ⬡
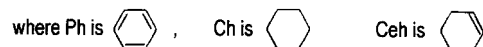
These results show that the lateral 3-methyl substitution of the 1,4-cyclohexenylene fragment results in the lowest value of nematic thermostability compared to those of the corresponding 3-methyl substituted *trans*-1,4-cyclohexylene and 1,4-phenylene fragments incorporated into the same molecular core (system **XVII**). The results presented reveal that the mesomorphic properties of laterally substituted 1,4-cyclohexenylene derivatives are influenced by their molecular structure, quantity, type and position of the lateral substituents.

2.4. *Lateral substitution of heterocyclic molecular fragments*

It has been shown that lateral substitution of the pyridin-2,5-diyl, pyrimidin-2,5-diyl and *trans*-1,3-dioxan-2,5-diyl fragments of the molecular core of liquid crystals leads to similar effects in their phase transition temperatures as in the case of lateral substitution of the 1,4-phenylene fragment [136, 161–163]. Some examples of laterally substituted heterocyclic liquid crystals and their parent compounds are given in table 13. The introduction of the chloro and fluoro atoms, and a methyl group in the lateral position of the pyridin-2,5-diyl or *trans*-1,3-dioxan-2,5-diyl fragments incorporated into

Table 13.   Mesomorphic properties of liquid crystals **13-1**–**13-9**.

No.	Compound	Phase transitions/°C	Reference
13-1		Cr59·3N94·6I	[136]
13-2		Cr76·8I	[136]
13-3		Cr231N(189)I	[136]
13-4		Cr117N265I	[21]
13-5		Cr137N158I	[21]
13-6		Cr37Sm94N179I	[19]
13-7		Cr60Sm91SmA124N150I	[161]
13-8		Cr113N204I	[159]
13-9		Cr106N128I	[160]
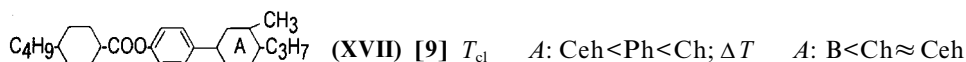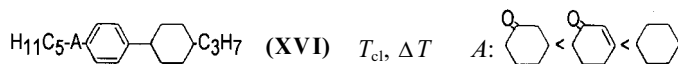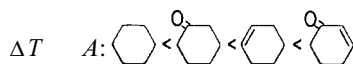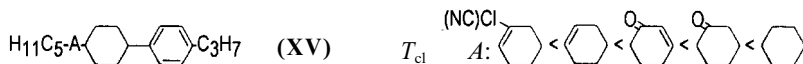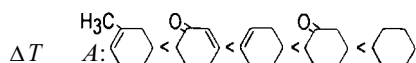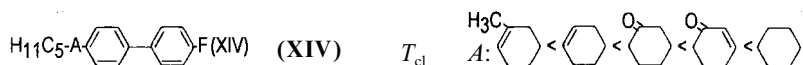
the molecular core of liquid crystals of given structures decreases the clearing temperatures (compounds **13-1** and **13-2**; **13-4** and **13-5**; **13-6** and **13-7**; **13-8** and **13-9**); can increase (compounds **13-1** and **13-2**; **13-4** and **13-5**; **13-6** and **13-7**) and decrease (compounds **13-8** and **13-9**) the melting temperatures, respectively; and can increase the smectic thermostability (compounds **13-6** and **13-7**).

The higher clearing and melting points of laterally hydroxy substituted pyridine derivatives compared to those of the corresponding laterally unsubstituted analogues can be explained in terms of increasing the axial molecular polarizability resulting from delocalization of π-electrons caused by intramolecular hydrogen bonding [136].

The influence of lateral hydroxy substitution on the alkoxy group's efficiency of the 2,5-disubstituted pyridine

derivatives can be derived as follows (see table 13 and [136]):

$$H_{2n+1}C_nO-\!\!\!\bigcirc\!\!\!-\!\!\!\bigcirc\!\!\!\underset{N\diagdown X}{\diagup CN} \qquad \textbf{(XVIII)}$$
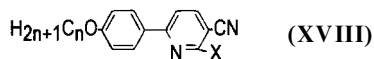
$$X = \text{H}, \quad T_{cl} \to n: n=5 < n=6 < n=7 < n=8$$

$$\Delta T \to n: n=8 < n=7 < n=6 \approx n=5$$

$$X = \text{OH}, \quad T_{cl} \to n: n=5 < n=6 < n=7 < n=8$$

$$\Delta T \to n: n=6 < n=7 < n=8$$

These results reveal that the lateral hydroxy substitution of the pyridin-2,5-diyl fragment of system **XVIII** affects the ordering of the nematic ranges and has no influence on the ordering of the clearing points in dependence on the alkoxy group's length.

The results presented in this section clearly show that the phase transition temperatures of laterally substituted heterocyclic liquid crystals strongly depend on their molecular structure, type and position of the lateral substituent.

3. Static dielectric properties

From dielectric theory of nematic liquid crystals the dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are, respectively, dielectric constants that are parallel and perpendicular to the nematic director **n**, is given by equation (1) [164]:

$$\Delta\varepsilon = NhF/\varepsilon_0 [\Delta\alpha - F\mu^2/kT(1-3\cos^2\beta)]S \qquad (1)$$

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

The introduction of lateral substituents into LC molecular structures has a considerable effect on their dielectric anisotropy (compounds **14-1** and **14-2**; **14-3**–**14-6**; **5-1** and **5-3**; see table 14). These results can be explained in terms of the contribution of the individual dipole moments of the lateral substituents to the overall molecular dipole moment relative to the director [equation (1)]. For example, when the longitudinal component of the dipole moment for the lateral substituent coincides with that for the terminal polar group, $\Delta\varepsilon$ grows (compounds **14-3**, **14-5**, **14-6**; **5-1** and **5-3**, table 14); in other case $\Delta\varepsilon$ decreases (compounds **14-3** and **14-4**).

It has been shown that liquid crystalline molecules having strongly polar end groups form associated pairs. Both head-to-head and head-to-tail pairing occurs [166–168], but antiparallel association predominates

and reduces the effective dipole moment [169]:

$$\mu_{\text{eff}}^2 = g\mu^2, \qquad (2)$$

$$\mu_{\text{eff}}^2 = \frac{9kT(\varepsilon_i - \varepsilon_i^\infty)(2\varepsilon_i + \varepsilon_i^\infty)}{4\pi N\varepsilon_i(\varepsilon_i^\infty + 2)^2}, \qquad (3)$$

where $\varepsilon_i^\infty = 1 \cdot 05 n_i^2$; g is the correlation factor characterizing the degree of association [169]:

It has been found that lateral fluoro substitution of 4-*n*-alkyl (or alkoxy)-4-cyanobiphenyl increases the value of g revealing the decrease of antiparallel associations in these systems [170, 171]. In the case of two-ring cyano benzoate esters, the effect of lateral fluoro substitution in the *ortho* position to the terminal CN group is to increase the correlation factors of upto $1 \cdot 4$ [171] providing evidence in support of the concept of parallel associations proposed in reference [167].

4. Optical properties

The phenomenological relation between the refractive index and the polarizability can be defined as [172, 173]:

$$(n^{*2}-1)/(n^{*2}+2) = N\alpha^*/3\varepsilon_0, \qquad (4)$$

where the mean polarizability $\alpha^* = (\alpha_\parallel + 2\alpha_\perp)/3$; $n^{*2} = (n_e^2 + 2n_o^2)/3$; n_o is the ordinary and n_e is the extra-ordinary refractive index. From equation (4) and previous section, it follows that the compounds which have a large induced polarizability of their highly conjugated π-electron system exhibit the large values of the optical anisotropy $\Delta n = n_e - n_o$.

As can be seen from table 14, the lateral fluoro substitution of compound **14-3** decreases its optical anisotropy (compounds **14-4** and **14-5**). 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 [174]:

5. Visco-elastic properties

It has been shown that liquid crystalline materials for TN and STN applications should have a low viscosity to give accceptable response times for LCDs [175, 176]. The following examples and the data collated in the literature [2–4, 6, 10, 20] reveal that lateral substitution of nematic systems always leads to increased rotational γ_1 and kinematic v viscosities, see compounds **14-3**, **14-5**, **14-6**; **14-7** and **14-8**, table 14.

The elastic constant ratio K_3/K_1 is a parameter of great importance for STN-LCDs defining their electro-optical performance [177]. It has been found that lateral fluoro substitution of the 1,4-phenylene fragment incorporated into the molecular core of liquid crystals has a significant effect on their elastic properties depending on their molecular structure, position and

Table 14. Dielectric, optical and visco-elastic properties of liquid crystals **14-1**–**14-10**, **5-1** and **5-3**.

No.	Compound	$\Delta\varepsilon$	Δn	$v/mm^2\,s^{-1}$	K_3/K_1	Reference
14-1	H_7C_3–◯–◯–COO–◯–C_3H_7	-0.32[a]				[10]
14-2	H_7C_3(with H$_3$C)–◯–◯–COO–◯–C_3H_7	-0.74[a]				[10]
14-3	H_7C_3–◯–◯–◯–F	3.6[b]	0.097[c]	16[c]		[90, 165]
14-4	H_7C_3–◯–◯–◯–F (F)	1.2[b]				[165]
14-5	H_7C_3–◯–◯–◯–F,F	4.0[b]	0.089[c]	21[c]	1.6[e]	[34, 90, 165]
14-6	H_7C_3–◯–◯–◯–F,F,F	4.3[b]	0.073[h]	25.1[h]	1.4[e]	[34, 165]
14-7	$H_{11}C_5$–◯–◯–◯(N)–C_3H_7			60[d]		[19, 64]
14-8	$H_{11}C_5$(H$_3$C)–◯–◯–◯(N)–C_3H_7			95[f]		[11, 64]
14-9	$H_{11}C_5$–◯–COO–◯–C_5H_{11}				0.68[g]	[178]
14-10	$H_{11}C_5$–◯–COO–◯(F)–C_5H_{11}				1.13[g]	[178]
5-1	$H_{11}C_5$–◯(O,B,O)–◯–COO–◯–CN	18.5[e]				[8]
5-3	$H_{11}C_5$–◯(O,B,O)–◯–COO–◯(F)–CN (F)	46[e]				[8]

a: $\tau = T/T_{N-I} = 0.9$; T/K, T_{N-I}/K. b: $\tau = 0.85$. c and d: extrapolated from the 10 % w/w solutions in ZLI-4792 and ZLI-3086, respectively, at 20°C. e: $T = T_{N-I} - 60$°C. f: $T = 20$°C. g: $\tau = 0.95$. h: extrapolated from the 20 % w/w solution in the mixture of 3,4-difluoro-substituted derivatives at 20°C.

type of lateral substituent. Lateral fluoro substitution of the 1,4-phenylene fragment incorporated into the molecular core of polar liquid crystals can decrease the K_3/K_1 ratio (compounds **14-5** and **14-6**), while the lateral fluoro substitution of the 1,4-phenylene fragment of weakly polar liquid crystals can increase the elastic constant ratio (compounds **14-9** and **14-10**) [34, 178].

6. Electro-optical properties

The relationship between the type of lateral substituent and the electro-optical parameters of liquid crystalline mixtures containing laterally substituted compounds can be found from the data presented in table 15. The coincidence of the direction of longitudinal parts of the dipole moments of lateral substituents with the direction of the dipole moment of terminal CN group gives rise to the total dipole moment, and consequently to the dielectric anisotropy [see equation (1)], which results in decreasing the threshold voltage of the twist-

effect [179] of liquid crystalline mixtures **2**–**5** and **7**–**9** compared to those of mixtures **1** and **6** containing corresponding laterally unsubstituted analogues, respectively [22], see also [11, 15–17, 19].

7. Conclusions

In this work, lateral substitution in nematic systems has been summarized with reference to their physico-chemical and electro-optical properties which are strongly dependent on their molecular structure, quantity, type and position of the lateral substituents. The results presented demonstrate that lateral substitution of the fragments incorporated into the molecular core of liquid crystals can provide desirable variations in their meso-morphic, dielectric, optical and elastic properties for improved satisfaction of the requirements for using them as the components of liquid crystalline materials for different display applications.

Table 15. Electro-optical properties of liquid crystalline mixture [22]:

$$H_{11}C_5\text{-}A\text{-}\bigcirc\text{-COO-}\bigcirc\begin{smallmatrix}X\\CN\end{smallmatrix}\qquad \textbf{(XIX)}$$
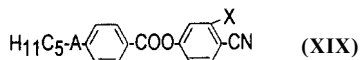
N	A	X	Threshold voltage V_{10}/V 25°C	Saturation voltage V_{90}/V 25°C
1	Ch	H	2·80	4·00
2	Ch	F	2·24	2·96
3	Ch	Cl	2·25	3·37
4	Ch	Br	2·23	3·35
5	Ph	CH$_3$	2·66	3·38
6	Ph	H	2·74	3·90
7	Ph	F	2·01	2·90
8	Ph	Cl	2·32	3·36
9	Ph	CH$_3$	2·67	3·41

Ch is the *trans*-1,4-cyclohexylene group; Ph is the 1,4-phenylene group; Liquid crystalline mixtures are composed of 25% w/w of the 4-ethoxyphenyl *trans*-4-butylcyclohexyl-carboxylate, 55% w/w of the 4-ethoxyphenyl *trans*-4-hexylcyclohexanecarboxylate and 20% w/w of a compound belonging to the system (**XIX**) [22].

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