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## Liquid Crystals

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### Nitrogen-containing fused heterocycles as the structural fragments in calamitic liquid crystals

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# Nitrogen-containing fused heterocycles as the structural fragments in calamitic liquid crystals

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This review examines in some detail the effect of introducing nitrogen-containing fused heterocycles into the molecular core of calamitic liquid crystals on their physico-chemical properties. The results of this study are compared with those obtained for other molecular fragments, and are rationalized in terms of existent theories.

## 1. Introduction

The present boom in liquid crystal display (LCD) technology is powered by the progress made in research on liquid crystalline materials. It has been demonstrated that one of the important prerequisites for the development of LC materials for display applications is the definition of the structure–property relationships for the liquid crystals [1–5]. In continuation of our work on LC structure–property relationships (see, for example [5–10]), the effect on their physico-chemical properties of introducing nitrogen-containing fused heterocycles into the molecular core of calamitic liquid crystals will be reviewed, rationalized in terms of existent theories, and compared with the effect of other well-known molecular fragments.

In order to avoid additional effects on the molecular polarizability and flexibility [11, 12] and on the efficiency of molecular fragments [6, 8, 9], it was decided to study laterally unsubstituted liquid crystalline derivatives having only single carbon–carbon bonds between their rings.

## 2. Mesomorphic properties

It would be better to estimate the effect of introducing nitrogen-containing fused heterocycles into the molecular core of liquid crystals having the same terminal substituents. However, the available data in the literature make this difficult. Hence, several combinations of the terminal substituents will be used for reviewing the mesomorphic properties of calamitic liquid crystals incorporating nitrogen-containing fused heterocycles and other molecular fragments.


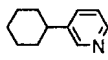













### 2.1. Bicyclic fragments

#### 2.1.1. 5,6,7,8-Tetrahydroquinolin-2,6-diyl

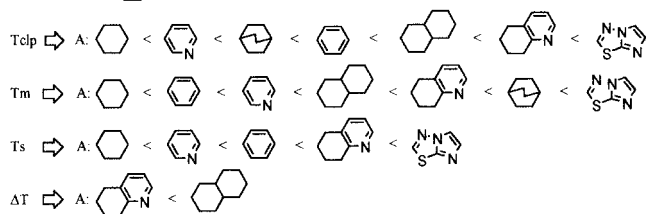
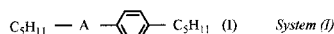
It has been shown that the pyridin-2,5-diyl [5, 7, 13–20] and *trans*-1,4-cyclohexylene [10] can be used as structural fragments in liquid crystals. The fusion of these two rings gives 5,6,7,8-tetrahydroquinoline [21] which was found to be a useful building unit of calamitic liquid crystals [5, 20, 22–26]. The effect of introducing the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of liquid crystals on their mesomorphic properties is shown in tables 1–7.

As can be seen from table 1, the weakly polar two-fragment 5,6,7,8-tetrahydroquinolin-2,6-diyl derivative exhibits the nematic–isotropic ( $T_{N-I}$ ) phase transition (compound **1-1**) which is considerably lower than that of the corresponding three-fragment derivative **1-2** containing non-fused *trans*-1,4-cyclohexylene and pyridin-2,5-diyl fragments. Replacing the 5,6,7,8-tetrahydroquinolin-2,6-diyl (consisting of pyridine [35–43] and cyclohexane [44, 45] moieties) in compounds **1-1** and **1-9** by other bicyclic and monocyclic fragments significantly lowers their clearing points (compounds **1-1** and **1-3–1-8**, **1-9** and **1-10–1-15**, except compound **1-13**, table 1). Particularly, the incorporation of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of two-fragment dipentyl derivatives increases the clearing and melting temperatures compared with those of the corresponding pyridin-2,5-diyl and *trans*-1,4-cyclohexylene derivatives (compounds **1-9** and **1-11**, **1-12**, see also compounds **1-1** and **1-4**, table 1). It is useful to express the effect of introducing the 5,6,7,8-tetrahydroquinolin-2,6-diyl fragment into the molecular core of liquid crystals in comparison with other well-known molecular fragments by the following orders of increasing

Table 1. Mesomorphic properties of liquid crystals:  $C_nH_{2n+1} - A - C_mH_{2m+1}$ 

Compound	$n$	A	$m$	Phase transitions/ $^{\circ}C$	Reference
<b>1-1</b>	3		5	Cr 55.4 N 66 I	[22, 25]
<b>1-2</b>	3		5	Cr 30 Sm 173 N 181 I	[27]
<b>1-3</b>	3		5	Cr <sub>2</sub> 33.2 Cr <sub>1</sub> 35 N 45.2 I	[28]
<b>1-4</b>	3		5	Cr 20 S (5) I	[25]
<b>1-5</b>	3		5	Cr - 18 Sm 47.8 I	[29]
<b>1-6</b>	3		5	Cr 81.5 I	[30]
<b>1-7</b>	3		5	Cr 76 I	[31]
<b>1-8</b>	3		5	Cr 57 I	[32]
<b>1-9</b>	5		5	Cr 43 Sm 72.7 N 73.6 I	[22, 25]
<b>1-10</b>	5		5	Cr 39.9 N 59.7 I	[28]
<b>1-11</b>	5		5	Cr 33 Sm (30.7) I	[25]
<b>1-12</b>	5		5	Cr - 0.8 Sm (- 8) N (- 5) I	[33]
<b>1-13</b>	5		5	Cr 95.6 Sm (89.4) I	[34]
<b>1-14</b>	5		5	Cr 26 SmE 47.6 SmB 52.2 I	[33]
<b>1-15</b>	5		5	Cr 52 N (33) I	[32]

clearing temperatures ( $T_{c1}$ ) (nematic–isotropic or smectic–isotropic phase transition temperatures), melting temperatures ( $T_m$ ) (crystal–smectic or crystal–nematic phase transition temperatures), smectic thermostabilities ( $T_s$ ) (smectic–nematic or smectic–isotropic phase transition temperatures), and nematic ranges ( $\Delta T$ ) depending on the type of molecular fragment A for the system (I):



These results reveal that the introduction of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of system (I) compounds produces liquid crystals exhibiting higher clearing and melting points, higher smectic thermostabilities and narrowest nematic ranges in comparison with those of other compounds of system (I) (except for the melting points of imidazo[2,1-b]-1,3,4-thiadiazol-2,6-diyl derivative **1-13**, and 1,4-bicyclo[2.2.2]-octylene derivative **1-15**).

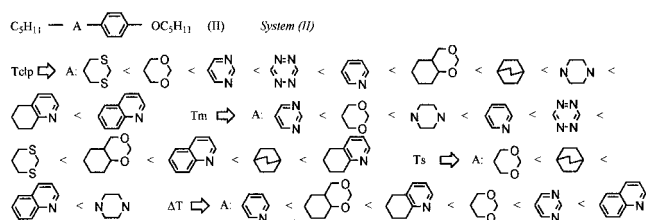
Similar results have been found for two-fragment pentyl-pentyloxy derivatives (table 2) showing higher clearing and melting points for the 5,6,7,8-tetrahydroquinolin-2,6-diyl derivative **2-1** in comparison with those of the corresponding compound incorporating pyridin-2,5-diyl (compound **2-4**) and other monocyclic fragments

Table 2. Mesomorphic properties of liquid crystals:  $C_nH_{2n+1} - A - OC_mH_{2m+1}$ .



Compound	$n$	A	$m$	Phase transitions/ $^{\circ}C$	Reference
2-1	5		5	Cr 87 N 99 I	[22, 25]
2-2	5		5	Cr 73 SmC 77 N 118 I	[46]
2-3	5		5	Cr 61 N 70 I	[47]
2-4	5		5	Cr 55 N 62 I	[25]
2-5	5		5	Cr 37 N 55.5 I	[48]
2-6	5		5	Cr 38 SmA (29) N 50.5 I	[49]
2-7	5		5	Cr 60 N (59.5) I	[50]
2-8	5		5	Cr 39.5 Sm <sub>1</sub> 54 Sm <sub>2</sub> 84.8 I	[51]
2-9	5		5	Cr 61 N (45) I	[52]
2-10	5		5	Cr 75 SmB (50) N (70.5) I	[32]
2-11	4		4	Cr 79 SmC 96 N 108 I	[80]
2-12	4		4	Cr 89 N 118 I	[53]
2-13	4		4	Cr 48 Sm 88 I	[14]
2-14	4		4	Cr 43 Sm 62 I	[14]
2-15	4		4	Cr 46.5 N (39.5) I	[48]
2-16	4		4	Cr 7.4 Sm 76 SmA 96.2 I	[54]















(compounds **2-5–2-10**), and the bicyclic *trans*-1,3-dioxadecalin-2,6-diyl fragment (compound **2-3**). A similar increase in the nematic–isotropic phase transition temperatures has been observed for the *trans*-1,3-dioxadecalin-2,6-diyl derivative **2-3** compared with that of compound **2-6** having a non-fused dioxan ring. It is interesting to note that 5,6,7,8-tetrahydroquinolin-2,6-diyl and *trans*-1,3-dioxadecalin-2,6-diyl derivatives, and the corresponding non-fused pyridin-2,5-diyl and *trans*-1,3-dioxan-2,5-diyl derivatives, show the same order of increase of the melting and clearing temperatures (compounds **2-1** and **2-3**, **2-4** and **2-6**, table 2). The replacement of the cyclohexane moiety by the benzene moiety in the 5,6,7,8-tetrahydroquinolin-2,6-diyl derivative **2-1**

creates the quinolin-2,6-diyl derivative **2-2** exhibiting a lower melting temperature, an additional smectic phase, and increased nematic range and thermostability:



From these results, it follows that the introduction of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular

Table 3. Physico-chemical properties of liquid crystals:  $C_nH_{2n+1}$    $($    $)_k$   $- A - C_mH_{2m+1}$ 

Compound	$n$	$k$	A	$m$	Phase transitions/ $^{\circ}C$	$d_1^a/\text{\AA}$	$\xi_1^a/\text{\AA}$	Reference
3-1	5	0		4	Cr 33 Sm (20) I			[22, 25]
3-2	5	0		4	Cr 31 N 44.8 I			[55]
3-3	3	1		5	Cr 96 Sm 116 N 209 I			[22, 25]
3-4	3	1		5	Cr 48 Sm 93.8 N 177.4 I			[18]
3-5	3	1		5	Cr 41 SmA 156 N 160 I			[34]
3-6	3	1		5	Cr 92 N 184 I			[56]
3-7	3	1		5	Cr 69 SmA 147.5 N 170.5 I			[34]
3-8	3	1		5	Cr 145 SmA 153 N 221 I			[34]
3-9	3	1		5	Cr 102 X <sup>b</sup> 142 I			[57]
3-10	2	1		3	Cr 86 Sm 92 N 201 I	21.6	70	[22, 23, 25]
3-11	2	1		3	Cr 144 Sm 191 N 315 I			[18]
3-12	2	1		3	Cr 51.9 Sm 92.7 N 158.8 I	19.5	48	[18, 23, 25, 58]
3-13	5	1		6	Cr 67 Sm 125 SmA 204 N 214 I			[59]
3-14	5	1		6	Cr 72.1 Sm <sub>1</sub> 81.9 Sm <sub>2</sub> 102.2 I			[60]

<sup>a</sup> Measuring temperature,  $T_{meas} = T_{N-1} - 40^{\circ}C$ .

<sup>b</sup> X is the unknown mesophase.

core of system (II) compounds produces liquid crystals showing moderate nematic range, high clearing temperatures and with the highest melting points among compounds belonging to this system.

Interestingly, the replacement of the 1,4-phenylene by the 5,6,7,8-tetrahydroquinolin-2,6-diyl, and the pentyl group by the butyl group, in the molecular structure of compound **1-12** (table 1) to give compound **3-1** (table 3) significantly increases the clearing and melting points, leading to the disappearance of a monotropic nematic phase and the creation of a monotropic smectic phase. Replacement of the pyridine moiety by the benzene moiety in the 5,6,7,8-tetrahydroquinolin-2,6-diyl fragment of compound **3-1** gives the corresponding 2,6-disubstituted

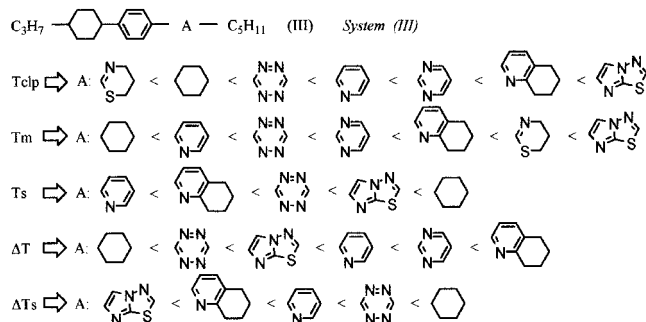
tetralin derivative **3-2** (table 3), exhibiting only the nematic phase with decreased melting and increased clearing temperatures.

As in the case of weakly polar two-fragment derivatives, the introduction of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of weakly polar three-fragment derivatives (compound **3-3**, table 3) results in an increase of the melting and clearing temperatures compared with those of the corresponding pyridin-2,5-diyl (compound **3-4**) and *trans*-1,4-cyclohexylene (compound **3-5**) derivatives, as well as of other corresponding derivatives containing the six-membered rings (compounds **3-6**, **3-7**). Compound **3-9** exhibits a higher melting point, and compound **3-8** shows the highest clearing

Table 4. Mesomorphic properties of liquid crystals:  $C_5H_{11} - A - C_6H_4 - CN$ .


Compound	A	Phase transitions/ $^{\circ}C$	Reference
4-1		Cr 96.2 N 98 I	[20, 22]
4-2		Cr 79.5 N 108.6 I	[55]
4-3		Cr 98 X 114 I	[61]
4-4		Cr 72.8 N 125.1 I	[28]
4-5		Cr 87 N (85) I	[47]
4-6		Cr 85.5 N 128 I	[62]
4-7		Cr 69 N 76 I	[62]
4-8		Cr 119.2 I	[34]
4-9		Cr 87 I	[63]
4-10		Cr 87.5 I	[64]
4-11		Cr 124 N 228 I	[19]
4-12		Cr 96 N 222 I	[65]
4-13		Cr 100.5 N 231 I	[66]
4-14		Cr 53.8 Sm 60.3 N 234.4 I	[67]
4-15		Cr 87 N 222.1 I	[68]
4-16		Cr 130 N 239 I	[69]











and melting temperatures among compounds belonging to the system (III):



These results show that the incorporation of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of system (III) compounds leads to the broadest nematic range with high thermostability, and moderate smectic thermostability and range ( $\Delta T_s$ ).

As was observed for weakly polar two-fragment derivatives, the weakly polar three-fragment 5,6,7,8-tetrahydroquinolin-2,6-diyl derivative (compound **3-10**, table 3) shows much higher melting and clearing temperatures than the corresponding pyridin-2,5-diyl derivative **3-12**, and lower melting and clearing points than the corresponding four-fragment compound **3-11** having non-fused pyridine and cyclohexane rings.

Table 5. Physico-chemical properties of liquid crystals: R — A —  CN, R = C<sub>5</sub>H<sub>11</sub>.

Compound	A	Phase transitions/°C	$d_{\lambda}^a$ /Å	$d_{\lambda}^a$ /Å	$\xi_{\lambda}^a$ /Å	$\xi_{\lambda}^a$ /Å	$\mu/D$ 25°C	$\varepsilon_{\perp}$ $\tau^b = 0.95$	$\Delta\varepsilon$ $\tau^b = 0.95$	$g$ $T_{N-1}$	$k_p$ 40°C	Reference
5-1		Cr 33.6 N 43.5 I					6.00	10.9	17.8	0.518	0.6538	[10, 17]
5-2		Cr 22.5 N 35 I					4.80	6.6 <sup>d</sup>	13.3 <sup>d</sup>	0.530 <sup>e</sup>	0.6523	[10, 70]
5-3		Cr 71 N (52) I					6.00	8.0 <sup>f</sup>	34.0 <sup>f</sup>	0.580		[10, 64]
5-4		Cr 30 N 55 I					4.63	5.3	11.2	0.590	0.6333	[10, 71]
5-5		Cr 56 N (49) I					6.00	8.0 <sup>f</sup>	17.4 <sup>f</sup>	0.585 <sup>e</sup>		[10, 49]
5-6		Cr 62 N 100 I					3.91		10.0 <sup>d</sup>	0.732	0.6590 <sup>e</sup>	[10, 72]
4-1 <sup>c</sup>		Cr 96.2 N 98 I					5.80	8.7	11.8	0.583	0.6754	[20, 22, 73]
5-7 <sup>c</sup>		Cr 67 N 98.1 I	20.2	29.3	33	60						[22, 25]
5-8 <sup>c</sup>		Cr 30.9 N 47 I	18.0	27.3	37	83						[17, 58]
5-9 <sup>c</sup>		Cr 30 N 59 I		30		60						[23, 71, 74]

<sup>a</sup>  $T_{m\text{eas}} = T_{N-1} = 10^{\circ}\text{C}$

<sup>b</sup>  $\tau = T_{m\text{eas}}/T_{N-1}$ ,  $k = 0.95$ .

<sup>c</sup> R = C<sub>7</sub>H<sub>15</sub>.

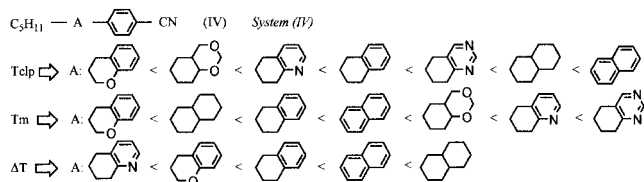
<sup>d</sup>  $\tau = 0.96$ .

<sup>e</sup> Extrapolated to  $T_{m\text{eas}} = T_{N-1}$  [208].

<sup>f</sup> Extrapolated from 10 wt % solution in ZLI-1132 at 20°C.

<sup>g</sup>  $T_{m\text{eas}} = 61^{\circ}\text{C}$ .

The data presented in table 4 show that the introduction of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of strong polar two-fragment cyano derivatives results in the formation of the nematic phase with moderate thermostability, high melting point and narrowest range (compounds **4-1** and **4-2–4-7**):



As was found above for weakly polar derivatives, the strong polar two-fragment 5,6,7,8-tetrahydroquinolin-2,6-diyl cyano derivative **4-1** exhibits substantially higher melting and clearing points than the corresponding pyridin-2,5-diyl cyano derivative **5-1** (table 5) and *trans*-1,4-cyclohexylene cyano derivative **5-4** (see also compounds **5-7** and **5-8**, **5-9**, table 5), and lower melting and clearing temperatures than the corresponding three-

fragment compound **4-11** (table 4) having non-fused cyclohexane and pyridine rings. Similar results were found for other liquid crystalline derivatives (compounds **4-2** and **5-2**, **5-4**, **4-12**; **4-3** and **5-3**, **5-4**, **4-13**; **4-4** and **5-4**, **4-14** (except melting point); **4-5** and **5-4**, **5-5**, **4-15** (the same melting point); **4-6** and **5-2**, **4-16**; tables 4, 5). Interestingly, this similar mesomorphic behaviour leads to different orders of increase of the clearing and melting temperatures observed for above mentioned compounds incorporating six-membered rings (system VI), the *trans*-1,4-cyclohexylene and the same six-membered rings (system V), and the corresponding fused fragments consisting of the cyclohexane and the same six-membered rings (system IV):

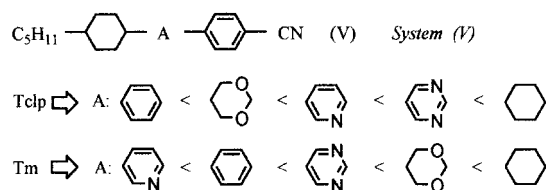
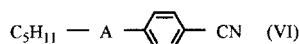
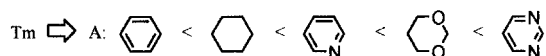
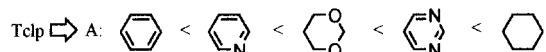


Table 6. Mesomorphic properties of liquid crystal:  $C_5H_{11} - A - \text{C}_6\text{H}_4 - X$ .

Compound	A	X	Phase transitions/ $^{\circ}C$	Reference
6-1		NCS	Cr 92 Sm 104 N 115.1 I	[20]
6-2		NCS	Cr 34 SmA 98.5 I	[20]
6-3		NCS	Cr 67.5 N (49.5) I	[75]
6-4		NCS	Cr 46 Sm 85.5 I	[76]
6-5		NCS	Cr 60 SmA 79 I	[77]
6-6		OCHF <sub>2</sub>	Cr 61.8 N (59.1) I	[20]
6-7		OCHF <sub>2</sub>	Cr 26 Sm 43.6 I	[20]
6-8		OCHF <sub>2</sub>	Cr 1 N (-17) I	[78]
6-9		OCHF <sub>2</sub>	Cr 20.1 Sm 24 I	[20]
6-10		OCHF <sub>2</sub>	Cr 23 Sm (4) N (8) I	[20]
6-11		F	Cr 65 N (55.1) I	[20]
6-12		F	Cr 28.1 I	[20]
6-13		F	Cr 31 I	[79]
6-14		OCHF <sub>2</sub>	Cr 121 N 204.1 I	[20]
6-15		OCHF <sub>2</sub>	Cr 69.5 Sm 119.6 N 167.5 I	[20]
6-16		OCHF <sub>2</sub>	Cr 37 SmB 102 N 170 I	[78]



System (VI)



















As was observed for weakly polar compounds, the introduction of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of two-fragment strongly polar cyano derivatives significantly increases the melting and clearing points compared with those of the corresponding cyano derivatives having six- and five-membered fragments (compounds **4-1** and **4-9**, **4-10**, **5-1-5-5**, tables 4, 5). While the imidazo[2,1-b]-1,3,4-thiadiazol-2,6-

diyl derivative **4-8** exhibits non-mesomorphic behaviour with a higher melting temperature, and the 1,4-bicyclo[2.2.2]-octylene derivative **5-6** shows a higher nematic thermostability.

Similar results have been found for other strongly polar (NCS terminally substituted) and moderately polar (OCHF<sub>2</sub>, F, OCF<sub>3</sub>) two- and three-fragment 5,6,7,8-tetrahydroquinolin-2,6-diyl derivatives which exhibit much higher melting and clearing temperatures than the corresponding pyridin-2,5-diyl, *trans*-1,4-cyclohexylene derivatives and other corresponding compounds having six-membered rings (compounds **6-1** and **6-2-6-5**; **6-6** and **6-7-6-10**; **6-11** and **6-12**, **6-13**; **6-14** and **6-15**, **6-16**; **7-1** and **7-2-7-5**; tables 6, 7).

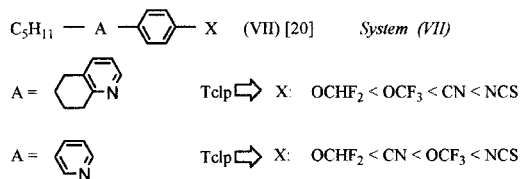


Table 7. Mesomorphic properties of liquid crystals:  $C_nH_{2n+1} - A - \text{C}_6\text{H}_4 - X$ .

Compound	$n$	A	X	Phase transitions/ $^{\circ}\text{C}$	Reference
7-1	5		$\text{OCF}_3$	Cr 57.5 N 63.2 I	[20]
7-2	5		$\text{OCF}_3$	Cr 18.6 SmB 38.5 SmA 52.4 I	[20]
7-3	5		$\text{OCF}_3$	Cr 14 I	[78]
7-4	5		$\text{OCF}_3$	Cr 32 SmA 45.2 I	[20]
7-5	5		$\text{OCF}_3$	Cr 23.6 SmB 34.9 I	[20]
7-6	5		$\text{OC}_2\text{H}_5$	Cr 73 X 105 I	[61]
7-7	6		$\text{OC}_4\text{H}_9$	Cr 40 N 53 I	[48]
7-8	6		$\text{OC}_4\text{H}_9$	Cr 48 SmA 88 I	[80]
7-9	6		$\text{OC}_4\text{H}_9$	Cr 49 SmC (43) N 57 I	[50]
7-10	6		$\text{OC}_4\text{H}_9$	Cr 50 Sm 54 N 61 I	[14]
7-11	6		$\text{OC}_4\text{H}_9$	Cr 48 Sm 85 I	[14]
7-12	6		$\text{OC}_4\text{H}_9$	Cr 35.5 SmA 44 N 50 I	[49]
7-13	6		$\text{OC}_4\text{H}_9$	Cr 20.8 Sm 54.5 SmA 83.4 I	[54]
7-14	6		$\text{OC}_4\text{H}_9$	Cr 40 SmB 78 I	[81]
7-15	6		$\text{OC}_4\text{H}_9$	Cr 55 N (44) I	[52]
7-16	6		$\text{OC}_4\text{H}_9$	Cr 55 I	[82]

The introduction of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of two- and three-fragment difluoromethoxy derivatives and two-fragment trifluoromethoxy derivatives shown in tables 6 and 7, respectively, creates only the nematic phase (compounds **6-6** and **6-14**, **7-1**), and promotes the nematic phase in two-fragment NCS derivatives (compound **6-1**) in comparison with the smectic character of the mesophases observed in the corresponding pyridine-2,5-diyl, pyrimidin-2,5-diyl, and *trans*-1,3-dioxan-2,5-diyl derivatives (except compound **6-10** showing both monotropic smectic and nematic phases) (compounds **6-1** and **6-2**, **6-4**, **6-5**; **6-6** and **6-7**, **6-9**; **7-1** and **7-2**, **7-4**, **7-5**; tables 6, 7).

It has been demonstrated that the replacement of the 5,6,7,8-tetrahydroquinolin-2,6-diyl by the pyridin-2,5-diyl in the molecular core of system (VII) compounds changes the efficiency of terminal groups [20]:



Similar results have been reported for other liquid crystalline 2,6-disubstituted 5,6,7,8-tetrahydroquinoline derivatives [5, 20, 22–26].

### 2.1.2. 5,6,7,8-Tetrahydroquinazolin-2,6-diyl

As can be seen from table 7, the introduction of the 5,6,7,8-tetrahydroquinazolin-2,6-diyl [83] into the molecular core of weakly polar two-fragment alkyl-alkoxy derivatives (compound **7-6**) (as it was shown before for the 5,6,7,8-tetrahydroquinolin-2,6-diyl alkyl-alkoxy derivatives presented in table 2) gives rise to clearing and melting temperatures comparable to those of the corresponding pyrimidin-2,5-diyl (compound **7-7**) and other six-membered ring derivatives (compounds **7-8–7-16**).

The data collated in table 4 and system (IV) show that the introduction of the 5,6,7,8-tetrahydroquinazolin-2,6-diyl into the molecular core of two-fragment cyano derivatives results in a moderate clearing point and the highest melting temperature among system (IV) compounds which, as was observed for the 5,6,7,8-tetrahydroquinolin-2,6-diyl cyano derivatives (see table 4), are higher than those of the corresponding pyrimidin-2,5-diyl, *trans*-1,4-cyclohexylene and other derivatives containing six- and five-membered rings (compounds **4-3** and **4-9**, **4-10**, **5-3–5-6**, tables 4, 5), and lower than those of the corresponding three-fragment cyano derivative incorporating non-fused cyclohexane and pyrimidine rings (compounds **4-3** and **4-13**, table 4).

Similar trends have been observed for other liquid crystalline 2,6-disubstituted 5,6,7,8-tetrahydroquinazoline derivatives [57].

### 2.1.3. Quinoline

The effect of the introduction of the quinoline fragment [39, 40, 43, 84–88] into the molecular core of calamitic liquid crystals is shown in tables 2, 8, 9. As in the case of weakly polar 5,6,7,8-tetrahydroquinolin-2,6-diyl derivatives, weakly polar 2,6-disubstituted quinoline derivatives exhibit higher melting and clearing temperatures than those of the corresponding 2,5-disubstituted pyridine derivatives (compounds **2-2** and **2-4**, **2-11** and **2-13**, **2-12** and **2-14**, **8-13** and **8-14**; tables 2, 8; system II).

It should be pointed out that the melting and clearing points of weakly polar two-fragment quinolin-2,6-diyl derivatives are also higher than those of the corresponding compounds incorporating 1,4-phenylene and other six-, five-membered rings and bicyclic fragments (compounds **2-11** and **2-14–2-16**; **2-12** and **2-13**, **2-15**, **2-16**; **8-13** and **8-15–8-17**; **9-13** and **9-11**, **9-12** (except melting point), **9-14–9-16**, tables 2, 8, 9).

Particularly, the incorporation of the quinolin-2,6-diyl into the molecular core of weakly polar two-fragment pentyl-pentyloxy derivatives (compound **2-2**, table 2; system II) gives the the smectic C phase with high melting point and high thermostability, and the broadest nematic phase with the highest thermostability among system (II) compounds.

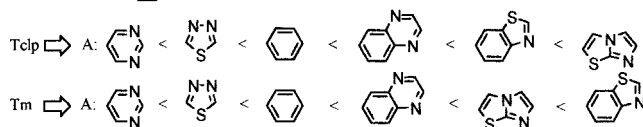
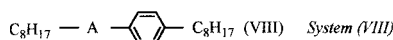
It has been demonstrated for liquid crystalline pyridine derivatives that the position of the nitrogen atom in the pyridine fragment, and its position in the molecular core, greatly influence the mesomorphic properties (compounds **2-13** and **2-14**, table 2; [7, 14, 15, 19, 102]). A similar relationship between the phase transition temperatures and the position of the nitrogen atom in the quinoline fragment and its position in the molecular core [53, 102] can be derived for liquid crystalline quinoline derivatives presented in table 2. The 3,7-disubstituted quinoline derivative **2-11** shows lower melting and clearing points and an additional smectic C phase in comparison with those of the corresponding 2,6-disubstituted quinoline derivative **2-12**. While for the corresponding 2,5-disubstituted pyridine derivatives **2-13** and **2-14**, the opposite behaviour of the phase transition temperatures has been found (table 2).

The data presented in table 8 reveal that the introduction of the quinolin-2,6-diyl into the molecular core of strongly polar two-fragment cyano derivatives results in the formation of the nematic phase that exhibits higher clearing and melting points than those of the corresponding 2,6-disubstituted naphthalene, 2,5-disubstituted pyridine, 2,5-disubstituted pyrimidine (except melting point), and 1,4-phenylene derivatives (compounds **8-1** and **8-2–8-4**, **5-2**, tables 5, 8).

Similar results have been obtained for other liquid crystalline derivatives incorporating the quinoline fragment [46, 53, 80, 89, 102–111].

### 2.1.4. Quinoxalin-2,6-diyl











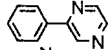






As can be seen from table 8, the introduction of the quinoxalin-2,6-diyl [41, 43, 112, 113] into the molecular core of weakly polar two-fragment dioctyl derivatives (compound **8-6**) creates only the smectic A phase exhibiting moderate melting temperature and moderate thermostability in comparison with those of corresponding compounds incorporating 1,4-phenylene, five-membered, and bicyclic fragments (compounds **8-5**, **8-7–8-10**)



As was observed above for the 2,6-disubstituted 5,6,7,8-tetrahydroquinoline and 5,6,7,8-tetrahydroquinazoline derivatives, two-fragment 2,6-disubstituted quinoxalin derivative **8-6** shows significantly lower melting and clearing temperatures than the corresponding non-fused three-fragment compound **8-11**.

Introducing the quinoxalin-2,6-diyl into the molecular core of two-fragment octyl-hexyloxy derivative **8-12** results in the same phase sequence with slightly reduced

Table 8. Mesomorphic properties of liquid crystals: X — A — Y.

Compound	X	A	Y	Phase transitions/ $^{\circ}\text{C}$	Reference
8-1	NC		$\text{C}_5\text{H}_{11}$	Cr 91.8 N 135.5 I	[89]
8-2	NC		$\text{C}_5\text{H}_{11}$	Cr 68 N 130 I	[90]
8-3	NC		$\text{C}_5\text{H}_{11}$	Cr 47.4 N 68 I	[7]
8-4	NC		$\text{C}_5\text{H}_{11}$	Cr 96 N 109 I	[64]
8-5	$\text{C}_8\text{H}_{17}$		$\text{C}_8\text{H}_{17}$	Cr 34 Sm (25) SmC 54.2 I	[91]
8-6	$\text{C}_8\text{H}_{17}$		$\text{C}_8\text{H}_{17}$	Cr 63.8 SmA 83.8 I	[80]
8-7	$\text{C}_8\text{H}_{17}$		$\text{C}_8\text{H}_{17}$	Cr 126 SmA 129 I	[80]
8-8	$\text{C}_8\text{H}_{17}$		$\text{C}_8\text{H}_{17}$	Cr 31.5 SmA 50.2 I	[80]
8-9	$\text{C}_8\text{H}_{17}$		$\text{C}_8\text{H}_{17}$	Cr 65 Sm <sub>1</sub> 85 Sm <sub>2</sub> 107 Sm <sub>3</sub> 120.5 SmC 149 I	[92]
8-10	$\text{C}_8\text{H}_{17}$		$\text{C}_8\text{H}_{17}$	Cr 57 Sm 61 I	[80]
8-11	$\text{C}_8\text{H}_{17}$		$\text{C}_8\text{H}_{17}$	Cr 104.6 SmC 178 SmA 187 I	[93]
8-12	$\text{C}_8\text{H}_{17}$		$\text{OC}_6\text{H}_{13}$	Cr 65.1 SmC 89 SmA 102.2 N 11.4 I	[94]
8-13	$\text{C}_8\text{H}_{17}$		$\text{OC}_6\text{H}_{13}$	Cr 69 SmC 104 SmA 113 N 117 I	[46]
8-14	$\text{C}_8\text{H}_{17}$		$\text{OC}_6\text{H}_{13}$	Cr 13.8 Sm 15 SmG 19 SmF 54 SmC 76.2 I	[95]
8-15	$\text{C}_8\text{H}_{17}$		$\text{OC}_6\text{H}_{13}$	Cr 46 Sm 84 I	[80]
8-16	$\text{C}_8\text{H}_{17}$		$\text{OC}_6\text{H}_{13}$	Cr 27.5 SmC 44.5 SmA 57.5 N 65 I	[48]
8-17	$\text{C}_8\text{H}_{17}$		$\text{OC}_6\text{H}_{13}$	Cr 39.3 SmA 64.2 I	[96]

phase transition temperatures than those of the corresponding quinolin-2,6-diyl derivative **8-13**, while the melting and clearing temperature of compound **8-12** are higher than those of the corresponding six-membered ring derivatives **8-14–8-17**. Similar trends have been observed for other liquid crystalline quinoxaline derivatives [114, 115].

















### 2.1.5. Benzoxazole

The fusion of the six-membered benzene and five-membered oxazole rings produces the benzoxazole frag-

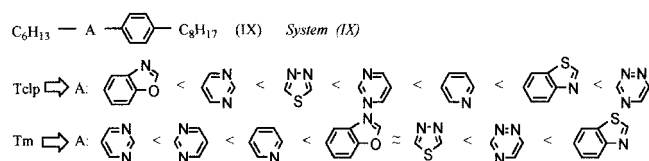
ment [37, 115–119] which can be used as the structural fragment in calamitic liquid crystals [13, 15, 80, 97, 120].

Table 9 presents the mesomorphic properties of some weakly polar two-fragment 2,5- and 2,6-disubstituted benzoxazole derivatives, with lower thermal stability of the mesophase observed for the latter compounds caused by increased molecular non-linearity [13, 15] (compounds **9-1** and **9-2**, see also **9-5**). Remarkably increased nematic thermostability of the corresponding 2,6-disubstituted benzothiazole derivative **9-3** has been explained in terms of increased conjugation of heteroatom p-electrons

Table 9. Mesomorphic properties of liquid crystals:  $C_nH_{2n+1}(O)_k - A - (O)_pC_mH_{2m+1}$ 

Compound	$n$	$k$	A	$p$	$m$	Phase transitions/ $^{\circ}C$	Reference
9-1	1	1		1	6	Cr 77.7 N (69.5) I	[13]
9-2	1	1		1	6	Cr 70.6 N (40.6) I	[13]
9-3	1	1		1	6	Cr 105.5 N 119.2 I	[13]
9-4	6	0		0	8	Cr 62 SmA 69 I	[59]
9-5	6	0		0	8	Cr 39.9 SmC (23) SmA (25.5) I	[97]
9-6	6	0		0	8	Cr 40 SmC 44.5 I	[91]
9-7	6	0		0	8	Cr 38 Sm 60.5 I	[98]
9-8	6	0		0	8	Cr 18 SmA 29.5 I	[99]
9-9	6	0		0	8	Cr 18.5 SmB 52 SmA 55.5 I	[99]
9-10	6	0		0	8	Cr 44 SmB 49 SmA 72 I	[80]
9-11	6	0		1	8	Cr 55 SmC 106 I	[59]
9-12	6	0		1	8	Cr 73 SmC 80 SmA 83 I	[100]
9-13	6	0		1	8	Cr 68 SmC 106 N 116 I	[46]
9-14	6	0		1	8	Cr 36 N 62 I	[48]
9-15	6	0		1	8	Cr 51 SmB 63 SmA 87 I	[80]
9-16	6	0		1	8	Cr 46 SmA 52.2 N 58 I	[49]



with  $\pi$ -electrons of the ring [13]. The introduction of the benzoxazol-2,5-diyl into the molecular core of two-fragment hexyl-octyl derivatives creates monotropic smectic C and A phases exhibiting moderate melting temperatures and the lowest clearing points among system (IX) compounds (compounds 9-5 and 9-4, 9-6–9-10, table 9):



















Similar results have been found for weakly polar three-fragment derivatives incorporating benzoxazol-2,5-diyl which show the lowest clearing point in comparison with that of other corresponding compounds having five- or six-membered fragments (compounds 10-1 and 10-2–10-6, table 10).

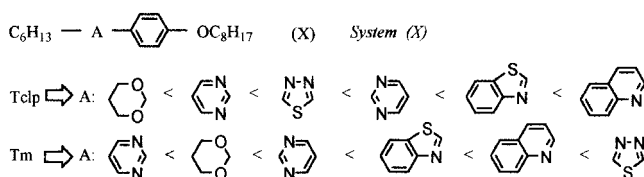
### 2.1.6. Benzothiazole

As can be seen from table 8, the introduction of the benzothiazol-2,6-diyl [43, 117, 128–132] into the molecular core of weakly polar two-fragment dioctyl derivatives creates a smectic A phase with the highest melting and high clearing temperatures among the

Table 10. Mesomorphic properties of liquid crystals:  $C_nH_{2n+1}(O)_k$ ——A—()<sub>p</sub>—X.

Compound	<i>n</i>	<i>k</i>	A	<i>p</i>	X	Phase transitions/°C	Reference
10-1	10	0		1	OC <sub>10</sub> H <sub>21</sub>	Cr 92.2 SmC 132.8 SmA 135.9 N 143.4 I	[121]
10-2	10	0		1	OC <sub>10</sub> H <sub>21</sub>	Cr 86 SmG 117.7 SmF 132.8 SmC 179.4 SmA 183.5 I	[122]
10-3	10	0		1	OC <sub>10</sub> H <sub>21</sub>	Cr 84 SmC 190 I	[123]
10-4	10	0		1	OC <sub>10</sub> H <sub>21</sub>	Cr 97 SmC 198 I	[123]
10-5	10	0		1	OC <sub>10</sub> H <sub>21</sub>	Cr 66 SmB 84 SmC 137 SmA 144.6 I	[100]
10-6	10	0		1	OC <sub>10</sub> H <sub>21</sub>	Cr 78 SmA 154 I	[63]
10-7	8	1		0	Br	Cr 75.5 SmE 107.5 N 149.5 I	[80]
10-8	8	1		0	Br	Cr 125.5 I	[124]
10-9	8	1		0	Cl	Cr 72 SmE 94.5 SmA 164 I	[80]
10-10	8	1		0	Cl	Cr 126 SmA 150 I	[125]
10-11	7	1		0	Cl	Cr 94 N 101 I	[126]
10-12	4	0		1	CN	Cr 157 SmA 197 N 274 I	[34]
10-13	4	0		1	CN	Cr 95 N 233 I	[19]
10-14	4	0		1	CN	Cr 93.5 N 244 I	[127]
10-15	4	0		1	CN	Cr <sub>2</sub> 69.5 Cr <sub>1</sub> 138 Sm 180 N 263 I	[127]
10-16	4	0		1	CN	Cr 144 SmC 192 N 261 I	[123]

corresponding 1,4-phenylene derivative and other system (VIII) compounds (compounds 8-7 and 8-5, 8-6, 8-8–8-10). Similar results were found for the systems (IX) and (X) (excepting the melting point which exhibits a moderate value) incorporating benzothiazol-2,6-diyl (compounds 9-4 and 9-5–9-10, 9-11 and 9-12–9-16, table 9; see also compounds 13-5 and 13-6–13-10, table 13):



As in the case of weakly-polar two-fragment systems, a three-fragment compound incorporating benzothiazol-2,6-diyl exhibits much higher clearing temperature than the corresponding derivative having five-membered fragment (compounds 3-13 and 3-14, table 3).

The data collated in table 10 show that the introduction of the benzothiazol-2,6-diyl into the molecular core of moderately polar two-fragment bromo and chloro derivatives considerably increases the clearing temperatures and lowers the melting points compared with those of the corresponding compounds having 1,4-phenylene and pyridazin-3,6-diyl fragments (compounds 10-7 and 10-8, 10-9 and 10-10).

Similar results have been seen for other liquid crystalline derivatives incorporating benzothiazole fragment [13, 105, 107, 133–138].

### 2.1.7. Benzotriazole

Recently, the use of benzotriazole [43, 117, 139–143] as a structural fragment in calamitic liquid crystals has been reported [143, 144]. As can be seen from table 10, the introduction of benzotriazol-2,6-diyl into the molecular core of two-fragment chloro derivatives creates a narrow nematic phase exhibiting high melting and clearing points (compound **10-11**). It has been demonstrated that the introduction of the benzotriazol-2,6-diyl into the molecular core of two- and three-fragment systems promotes the formation of the nematic phase in the case of aromatic systems [126] and creates a mesophase exhibiting highly smectic character in heterocyclic systems [144].

### 2.1.8. 1,3-Diaza-azulene

It has been reported that two- and three-fragment 2-substituted 1,3-diaza-azulene derivatives exhibit no mesophase in the case of weakly polar two-fragment compounds and strongly polar three-fragment nitro derivatives; and show high melting and clearing points in the case of weakly polar three-fragment compounds [145, 146].

### 2.1.9. Imidazo[2,1-b]thiazol-2,6-diyl

Starting from this paragraph some heterocyclic fused systems with one bridgehead nitrogen atom will be discussed. The first example of such systems is imidazo[2,1-b]thiazole [147, 148] which has recently been demonstrated as a structural fragment in calamitic liquid crystals [92]. As can be seen from table 8, the introduction of the imidazo[2,1-b]thiazol-2,6-diyl into the molecular core of weakly polar two-fragment dioctyl derivatives creates a number of smectic phases exhibiting high melting point and the highest clearing phases temperature among compounds of the system (VIII) (compounds **8-9** and **8-5-8-8, 8-10**). Similar trends have been found for other liquid crystalline imidazo[2,1-b]thiazol-2,6-diyl derivatives [92].

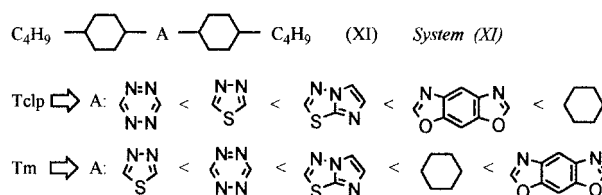
### 2.1.10. Imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl

The fusion of the imidazole and thiaziazole rings produces the imidazo[2,1-b][1,3,4]thiadiazole [148, 149] which has been used as a structural fragment in calamitic liquid crystals [34].

The data collated in table 1 show that the introduction of the imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl into the molecular core of weakly polar two-fragment dipentyl derivatives creates the monotropic smectic phase exhibiting the highest melting and clearing points, the highest

smectic thermostability among compounds of the system (I) (compounds **1-13** and **1-9-1-12, 1-14, 1-15**). Similar results for clearing and melting points were found for weakly polar three-fragment liquid crystalline derivatives incorporating imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl, while the smectic phase exhibits the narrowest range and high thermostability, and the nematic phase shows a moderate range among system (III) compounds (compounds **3-8** and **3-3-3-7, 3-9**, table 3).









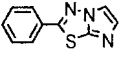
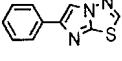
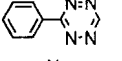





As can be seen from table 11, the introduction of the imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl as a middle fragment into the molecular core of weakly polar three-fragment di-*trans*-4-butylcyclohexyl derivatives creates smectic A and nematic phases exhibiting much higher melting and clearing temperatures (compound **11-1**) in comparison with those of the corresponding derivatives having 1,3,4-thiadiazol-2,5-diyl (compound **11-3**), or 1,2,4,5-tetrazin-3,6-diyl (compound **11-4**). The corresponding *trans*-1,4-cyclohexylene (compound **11-5**) and benzo[1,2-d:5,4-d']bisoxazol-2,6-diyl (compound **11-2**) derivatives show higher melting and clearing points:



Similar results were found for other weakly polar three-fragment dibutyl derivatives **11-6** and **11-7** incorporating the imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl as a middle fragment and the corresponding 1,3,4-thiadiazol-2,5-diyl derivative **11-8**. The influence of the position of the imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl in the molecular core of liquid crystals on their mesomorphic properties is well illustrated by comparing the phase transition temperatures of compounds **11-6** and **11-7**. Compound **11-6**, having the thiaziazole moiety of its imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl fragment connected with the butylcyclohexyl fragment, exhibits only the nematic phase. Compound **11-7**, with reversed structure of its imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl fragment, shows decreased clearing and melting points and an additional smectic A phase.

The introduction of the imidazo[2,1-b][1,3,4]thiadiazol-2,6-diyl into the molecular core of weakly polar four-fragment derivatives leads to the formation of mesophases exhibiting phase transition temperatures which are dependent on its position in the core and show the opposite behaviour to the previous results observed for three-fragment derivatives: only a nematic phase with lower clearing and melting temperatures was observed for compound **11-9** having the imidazole

Table 11. Mesomorphic properties of liquid crystals  $X - (\text{---})_k - (\text{---})_p - A - \text{---} - \text{C}_4\text{H}_9$ 

Compound	X	k	p	A	Phase transitions/°C	Reference
11-1	C <sub>4</sub> H <sub>9</sub>	1	0		Cr 103 SmA 164 N 177.5 I	[34]
11-2	C <sub>4</sub> H <sub>9</sub>	1	0		Cr 237 N 264 I	[150]
11-3	C <sub>4</sub> H <sub>9</sub>	1	0		Cr 39 Sm <sub>1</sub> 55 Sm <sub>2</sub> 64 SmB 162 I	[151]
11-4	C <sub>4</sub> H <sub>9</sub>	1	0		Cr 56 SmA 108 N 128 I	[34]
11-5	C <sub>4</sub> H <sub>9</sub>	1	0		Cr 104 Sm 265 I	[152]
11-6	C <sub>4</sub> H <sub>9</sub>	0	1		Cr 115 N 236 I	[34]
11-7	C <sub>4</sub> H <sub>9</sub>	0	1		Cr 114.5 SmA 151.5 N 195.8 I	[34]
11-8	C <sub>4</sub> H <sub>9</sub>	0	1		Cr 71 SmA 120 N 146 I	[151]
11-9	C <sub>3</sub> H <sub>7</sub>	1	0		Cr 126.5 N 273 I	[34]
11-10	C <sub>3</sub> H <sub>7</sub>	1	0		Cr 190 SmA 260 N 290 decomp.	[34]
11-11	C <sub>3</sub> H <sub>7</sub>	1	0		Cr 111 SmA 178 N 270 decomp.	[34]
11-12	NC	0	1		Cr 172.5 N 278 I	[34]
11-13	NC	0	1		Cr 132 N 202 I	[151]
11-14	NC	0	1		Cr 124 N 228 I	[19]
11-15	NC	0	1		Cr 118 N 234 I	[66]
11-16	NC	0	1		Cr 139.5 N 179.5 I	[66]

moiety connected with the *trans*-4-butylcyclohexyl fragment, compared with the existence of the smectic A and nematic phases of the corresponding derivative **11-10** with reversed structure of its imidazo[2,1-*b*][1,3,4]-thiadiazol-2,6-diyl fragment. As was shown for three-fragment compounds, weakly polar four-fragment imidazo[2,1-*b*][1,3,4]thiadiazol-2,6-diyl derivatives **11-9** and **11-10** exhibit higher melting and clearing temperatures than the corresponding 1,2,4,5-tetrazin-3,6-diyl derivative **11-11**.

The data presented in tables 4, 10, 11 show that the introduction of the imidazo[2,1-*b*][1,3,4]thiadiazol-2,6-diyl into the molecular core of strong polar two-fragment cyano derivatives creates no mesophases

(compound **4-8**), while three-fragment imidazo[2,1-*b*]-[1,3,4]thiadiazol-2,6-diyl cyano derivatives exhibit the highest melting and clearing temperatures in comparison with those of corresponding compounds incorporating the 1,3,4-thiadiazol-2,5-diyl fragment, and six-membered rings (compounds **10-12** and **10-13–10-16**, **11-12** and **11-13–11-16**). Similar results have been reported for other liquid crystalline imidazo[2,1-*b*][1,3,4]thiadiazol-2,6-diyl derivatives [34].

#### 2.1.11. *Thiazolo*[5,4-*d*]thiazol-2,5-diyl

It has been reported that 2,5-disubstitution by two long thiazolo[5,4-*d*]thiazole chains [153] creates no mesophase [154]. However the introduction of the

thiazolo[5,4-d]thiazol-2,5-diyl as a middle fragment into the molecular core of weakly polar three-fragment bihexyl derivatives creates the smectic E, smectic C and nematic phases showing high melting points and the highest clearing temperature among compounds presented in table 12 including thiazol-2,5-diyl and thiazol-2,4-diyl derivatives (compounds **12-1** and **12-2–12-15**, see also compounds **14-2** and **14-3–14-9**, tables 12, 14). Interestingly, compound **12-1** exhibits higher melting and clearing points than the corresponding four-fragment derivative **12-4** having two non-fused thiazole fragments.



Similar results have been seen for other liquid crystalline derivatives incorporating thiazolo[5,4-d]thiazole [154–156].

## 2.2. Tricyclic fragments

### 2.2.1. Benzo[1,2-d:5,4-d']bisoxazol-2,6-diyl

The effect on their mesomorphic properties of introducing benzo[1,2-d:5,4-d']bisoxazol-2,6-diyl into the molecular core of calamitic liquid crystals is revealed by consideration of the thermal data in tables 11–13.

As can be seen from table 13, 2,6-dihexyl substitution of the benzo[1,2-d:5,4-d']bisoxazole (which is the product of fusion of benzene and two oxazole rings) does not produce any mesophase (compound **13-1**); in contrast to the corresponding derivatives incorporating other tricyclic fragments **13-2** and **13-3** which exhibit the nematic phase and non-mesomorphic behaviour with a higher melting point, respectively. The introduction of the benzo[1,2-d:5,4-d']bisoxazol-2,6-diyl

Table 12. Mesomorphic properties of liquid crystals: C<sub>6</sub>H<sub>13</sub>  A  C<sub>6</sub>H<sub>13</sub>.




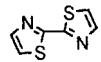










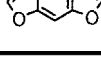
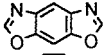
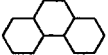
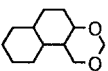
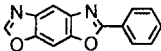
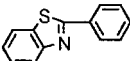
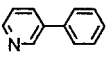
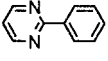
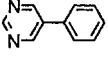
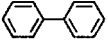
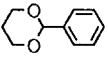
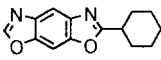
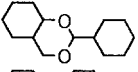
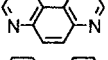
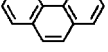
Compound	A	Phase transitions/°C	Reference
<b>12-1</b>		Cr 142 SmE (135) SmC 194 N 224 I	[155]
<b>12-2</b>		Cr 68.8 SmA 116.5 N 120 I	[157]
<b>12-3</b>		Cr 94 I	[158]
<b>12-4</b>		Cr 138 SmA 190 I	[158]
<b>12-5</b>		Cr 89 SmA 137 N 154 I	[63]
<b>12-6</b>		Cr 150 I	[159]
<b>12-7</b>		Cr 193 Sm 218 I	[160]
<b>12-8</b>		Cr 104 SmA 185 I	[161]
<b>12-9</b>		Cr 116.1 SmC 172.3 SmA 179.2 I	[93]
<b>12-10</b>		Cr 128 SmC 179 SmA 183 N 188 I	[123]
<b>12-11</b>		Cr 156.5 N 157.5 I	[162]
<b>12-12</b>		Cr 55 Sm 184 I	[152]
<b>12-13</b>		Cr 70 Sm 112 I	[152]
<b>12-14</b>		Cr 177.5 I	[163]
<b>12-15</b>		Cr 291 I	[150]



Table 13. Mesomorphic properties of liquid crystals:  $C_nH_{2n+1}(O)_k - A - (O)_pC_mH_{2m+1}$ 

Compound	$n$	$k$	A	$p$	$m$	Phase transitions/ $^{\circ}C$	Reference
13-1	6	0		0	6	Cr 58 I	[150]
13-2	6	0		0	6	Cr <sub>2</sub> 70 Cr <sub>1</sub> 75 N 87.5 I	[164]
13-3	6	0		0	6	Cr 61.5 I	[165]
13-4	6	0		0	6	Cr 144 I	[150]
13-5	6	0		0	6	Cr 54 SmA (45) N 56 I	[59]
13-6	6	0		0	6	Cr 25 Sm 52.5 I	[14]
13-7	6	0		0	6	Cr 29 I	[99]
13-8	6	0		0	6	Cr 30 SmB 42.5 SmA 53 I	[99]
13-9	6	0		0	6	Cr 35 SmBe 39.5 SmB 53.5 I	[96]
13-10	6	0		0	6	Cr 36.5 SmB 38.5 I	[49]
13-11	6	0		0	4	Cr 90 SmA 96 N 106 I	[150]
13-12	6	0		0	4	Cr 67.5 SmA 86.8 I	[47]
13-13	6	1		1	6	Cr 91 I	[166]
13-14	6	1		1	6	Cr 114 Sm 125 I	[167]

into the molecular core of weakly polar two-fragment aromatic derivatives again creates no mesophase (compound **13-4**); in contrast to the corresponding derivatives incorporating benzothiazol-2,6-diyl (compound **13-5**), 1,4-phenylene (compound **13-9**) and other monocyclic (compounds **13-6–13-8**, **13-10**) fragments exhibiting mesomorphic (compounds **13-5**, **13-6**, **13-8–13-10**) or non-mesomorphic behaviour (compound **13-7**) with considerably lower melting points. Similar high melting non-mesomorphic behaviour was observed for the three-fragment aromatic benzo[1,2-d:5,4-d']bisoxazol-2,6-diyl derivative **12-15** presented in table 12, while the incorporation of benzo[1,2-d:5,4-d']bisoxazol-2,6-diyl into the molecular core of weakly polar two- and three-fragment non-aromatic systems leads to the formation of mesophases showing the highest melting and clearing

points (among two-fragment compounds **13-11** and **13-12**, table 13) and the highest melting temperature and high nematic thermostability (among three-fragment compounds **11-2** and **11-1**, **11-3–11-5**, table 11).

Similar results have been reported for other liquid crystalline 2,6-disubstituted benzo[1,2-d:5,4-d']bisoxazole derivatives [150].

### 2.2.2. 1,8-Diazaphenanthren-2,7-diyl

The data presented in table 13 show that 2,7-dihexyloxy substitution of 1,8-diazaphenanthrene [168, 169] does not produce any mesophase (compound **13-13**) in contrast to the corresponding phenanthrene derivative **13-14** which exhibits high melting smectic behaviour. Similar results have been found for other 1,8-diazaphenanthren-2,7-diyl derivatives [166].

## 2.2.3. Benzo[1,2-d:4,5-d']bisthiazol-2,6-diyl

As can be seen from table 14, the introduction of benzo[1,2-d:4,5-d']bisthiazol-2,6-diyl as a central fragment into the molecular core of weakly polar three-fragment dioctyloxy derivatives creates some mesophases exhibiting the highest smectic and nematic thermostabilities (compound **14-1**) compared with those of the corresponding derivatives having thiazolo[5,4-d]thiazol-2,5-diyl (compound **14-2**), and monocyclic fragments (compounds **14-3–14-9**). Similar trends have been found for other liquid crystalline benzo[1,2-d:4,5-d']bisthiazol-2,6-diyl derivatives [170].

The effect on their mesomorphic properties of introducing nitrogen-containing fused heterocycles and other molecular fragments into the molecular core of calamitic liquid crystals can be correlated with the predominant influence of the packing of their molecules [33, 189] which depends on the structure and size of nitrogen-containing fused heterocycles [21, 37, 39, 40, 41, 43, 83–88, 112, 113, 116–119, 129, 130, 139–143, 147–149, 153, 168, 169, 172–174] and other molecular fragments [36–38, 40–45, 87, 117, 128, 129, 131, 132, 175, 188].



The anisotropic dispersion interactions, and consequently the anisotropy of polarizability, depending on the electron density distribution in the molecular fragments under investigation, also influence the packing and hence the stability of the mesophases but play a secondary role compared with the steric factors [189]. Other molecular aspects, such as the association [190]

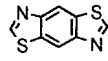








or dipole–dipole attraction in polar liquid crystalline derivatives, which can influence the packing of the molecules also affect the stability of the mesophases [189].

## 2.3. X-ray data

It has been shown that X-ray diffraction (XRD) of the nematic phase of liquid crystals is a useful method for studying the effects of the association of LC molecules on the structure of their nematic phases and consequently on the properties of liquid crystals formed by these molecules [58, 74, 191–193].

The investigation of polar liquid crystals by XRD 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  $d$ . They involve swarms containing tens to hundreds of molecules and are characterized by a correlation length  $\xi$  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 [58, 74, 191, 193]. 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 period  $d$ , for some other cyano derivatives belonging to various chemical classes show that  $d$

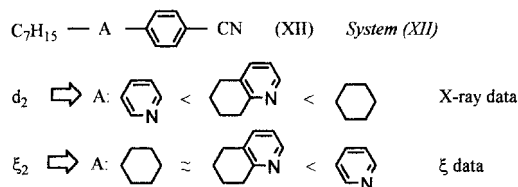
Table 14. Mesomorphic properties of liquid crystals:  $C_8H_{17}O$   A   $OC_8H_{17}$ .

Compound	A	Phase transitions/ $^{\circ}C$	Reference
<b>14-1</b>		SmG 259 SmC 339.5 N 344 I	[170]
<b>14-2</b>		Cr 105 SmE 153 SmC 240 N 246 I	[155]
<b>14-3</b>		Cr 101 SmC 194 N 196 I	[100]
<b>14-4</b>		Cr <sub>2</sub> 81.8 Cr <sub>1</sub> 107.3 SmC 149 N 157.3 I	[171]
<b>14-5</b>		Cr 141 SmC 183.4 SmA 192.8 I	[171]
<b>14-6</b>		Cr 118.8 SmB 121.1 SmC 209 I	[80]
<b>14-7</b>		Cr 131 Sm 187.5 N 195 I	[162]
<b>14-8</b>		Cr 163 Sm 203 I	[152]
<b>14-9</b>		Cr 86 SmC 213 I	[123]

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. Further XRD investigations 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  $L < d_2 < 2L$  [58, 74, 191, 193].

It has been shown that for two-fragment *trans*-1,4-disubstituted cyclohexylene cyano derivatives, only one density wave with a characteristic period  $d_2$  is observed [23, 58, 74] (compound **5-9** table 5), while the corresponding pyridin-2,5-diyl cyano derivative **5-8** exhibits two incommensurate density waves: monomeric with period  $d_1$  (period  $d_1$  is related to the fluctuation layer structure formed by separate molecules) and dimeric with decreased values of period  $d_2$  [23, 58, 74]. X-ray data presented in table 5 reveal that cyano derivative **5-7**, which has the 5,6,7,8-tetrahydroquinolin-2,6-diyl fragment consisting of cyclohexane and pyridine moieties, has a nematic phase structure which is closer to that of the pyridin-2,5-diyl cyano derivative, since it exhibits two incommensurate density waves.

As can be seen from table 5, the  $d_2$  values for two-fragment cyano derivatives differ significantly, indicating different degrees of molecular core overlap in the dimer formation [190, 194]. The different  $d_2$  values probably result from significantly different electron density distributions in the molecular structure (for the pyridine derivatives this is shown in [195]) and steric factors which are responsible for the type of dimerization. This can be expressed by the following order of increasing  $d_2$  depending on the type of molecular fragment A:



These results show that the 5,6,7,8-tetrahydroquinolin-2,6-diyl cyano derivative takes the intermediate position between the corresponding pyridin-2,5-diyl and *trans*-1,4-cyclohexylene cyano derivatives in the degree of their molecular overlap in the dimer formation.

It has also been demonstrated that the correlation length  $\xi$  characterizes the potential smectogenicity of nematic liquid crystals [56, 74, 193]. For the system (XII) the potential smectogenicity grows depending on the type of the molecular fragment A as shown above. These results reveal that two-fragment 5,6,7,8-tetrahydroquinolin-2,6-diyl cyano derivative **5-7** exhibits lower smectogenicity compared with that of the pyridin-2,5-diyl cyano derivative.

For the weakly polar compounds **3-10** and **3-12** (table 3), only the monomeric density wave was observed with a characteristic period  $d_1$ . The higher value of  $d_1$  for compound **3-10** corresponds to an increase in length in replacing the pyridin-2,5-diyl (compound **3-12**) by the 5,6,7,8-tetrahydroquinolin-2,6-diyl which also results in increasing the correlation length.

### 3. Static dielectric properties

The relationship between the dielectric anisotropy ( $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ , where  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  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 [196]:







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

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,  $\mu$  is the dipole moment,  $\beta$  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 properties of liquid crystals with different nematic-isotropic phase transition temperatures  $T_{N-1}$  can only be made at constant reduced temperature  $\tau = T_{meas}/T_{N-1}$  [197]. Tables 5 and 15 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 [197], the extrapolations are not meaningful, however these estimates are the only way to obtain a rough definition of the dielectric properties of non-mesomorphic compounds, smectic liquid crystals, and liquid crystals with a narrow nematic range.

The data on the dielectric properties of compounds and binary mixtures presented in tables 5 and 15 show that the replacement of the 5,6,7,8-tetrahydroquinolin-2,6-diyl by the 1,4-phenylene, pyridin-2,5-diyl or pyrimidin-2,5-diyl, increases the dielectric anisotropy due to the dipole moment (except compound **5-2**) and molecular polarizability being increased (compounds **4-1** and **5-1-5-3**, mixtures **15-1** and **15-2**, **15-4**, **15-6**, tables 5, 15). A similar increase in  $\Delta\epsilon$  is observed for *trans*-1,3-dioxan-2,5-diyl cyano derivatives (compound **5-5**, mixture **15-5**); while replacing the 5,6,7,8-tetrahydroquinolin-2,6-diyl by *trans*-1,4-cyclohexylene and 1,4-bicyclo[2.2.2]-octylene decreases the dielectric anisotropy by decreasing the dipole moment (compounds **4-1** and **5-4**, **5-6**; mixtures **15-1** and **15-3**, tables 5, 14). These results are found to

Table 15. Physico-chemical properties of binary mixtures ( $C_5$  and  $C_7 = 40:60$  mol %) of the liquid crystals:  $R - A - \text{C}_6\text{H}_4 - \text{CN}$ .

Compound	A	$T_{N-1}/^{\circ}\text{C}$	$\varepsilon_{\perp}^a$	$\Delta\varepsilon^a$	$\Delta\varepsilon/\varepsilon_{\perp}^a$	$\Delta n^a$	Reference
15-1		98.1	7.5	10.7	1.43	0.155	[5, 24]
15-2		44.1	10.7	16.0	1.50	0.175	[5, 10]
15-3		56.4	5.4	9.2	1.71	0.100	[5, 10]
15-4		39.0	6.0	11.7	1.95	0.184	[5, 10]
15-5		49.8	8.9 <sup>b</sup>	13.3 <sup>b</sup>	1.38 <sup>b</sup>	0.089 <sup>b,c</sup>	[198, 199]
15-6		51.0	8.7	19.6	2.86	0.174	[5, 10]

<sup>a</sup>  $\tau = T_{\text{meas}}/T_{N-1}$ ,  $K = 0.95$ .

<sup>b</sup>  $T_{\text{meas}} = T_{N-1} - 10^{\circ}\text{C}$ .

<sup>c</sup>  $\lambda = 520$  nm.

be in agreement with the equation (1) [196]. Similar effects on the dielectric properties of introducing the 5,6,7,8-tetrahydroquinolin-2,6-diyl and imidazo[2,1-b]-1,3,4-thiadiazol-2,6-diyl into molecular cores of other liquid crystalline derivatives have been found in [20, 24, 25] and [34], respectively.

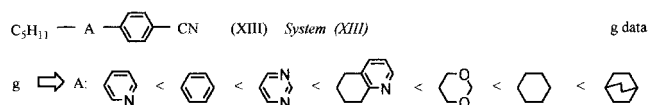
It has been shown that mesogenic molecules possessing strongly polar terminal groups form associated pairs. Both head-to-head and head-to-tail pairing occurs [194, 200–202], but antiparallel association predominates and reduces the effective dipole moment [190]:

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

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

where  $\varepsilon_i^{\infty} = 1.05n_i^2$  and  $g$  is the correlation factor characterizing the association tendency. For non-associating systems  $g$  is equal to 1. The data collated in table 4 reveal that all compounds under investigation exhibit values of  $g$  which are smaller than 1, indicating an antiparallel association. Replacement of the 5,6,7,8-tetrahydroquinolin-2,6-diyl by 1,4-phenylene, pyridin-2,5-diyl, pyrimidin-2,5-diyl and *trans*-1,4-cyclohexylene, *trans*-1,3-dioxan-2,5-diyl or 1,4-bicyclo[2.2.2]-octylene decreases the factor  $g$  (compounds **4-1** and **5-1–5-3**, table 5) or increases factor  $g$  (compounds **4-1** and **5-4–5-6**, table 5), respectively. In terms of association tendency, two-fragment 5,6,7,8-tetrahydroquinolin-2,6-diyl cyano derivative **4-1** is closer to the *trans*-1,4-cyclohexylene derivative **5-4** than to the pyridin-2,5-diyl derivative **5-1**.

These results can be expressed by the following orders of increasing  $g$  (table 5):

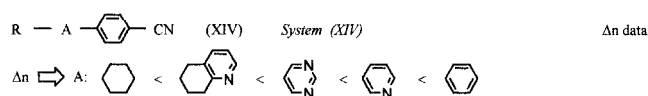


#### 4. Optical properties

The phenomenological relationship between the refractive index and the electric polarization is defined as [203, 204]:

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

where the mean polarizability  $\alpha^* = (\alpha_{\parallel} + 2\alpha_{\perp})/3$ ; the mean refractive index  $n^{*2} = (n_o^2 + 2n_e^2)/3$ ; and  $n_o$  is the ordinary and  $n_e$  the extraordinary refractive index, respectively. From equation (4) and the previous section, it follows that aromatic compounds which have a large induced polarizability of their highly conjugated  $\pi$ -electron system exhibit an optical anisotropy ( $\Delta n = n_e - n_o$ ) which is much larger than that of the corresponding 2,6-disubstituted 5,6,7,8-tetrahydroquinoline cyano derivative (mixtures **15-1** and **15-2**, **15-4**, **15-6**, table 15); while the corresponding *trans*-1,4-disubstituted cyclohexylene cyano derivatives (mixture **15-3**) show the lowest value of the  $\Delta n$ :



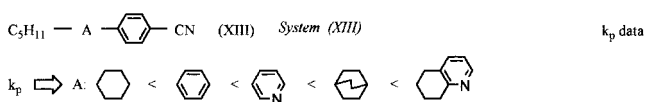
### 5. Molecular packing

It has been shown that liquid crystal molecular packing plays a very important role in the creation of their mesophases [33, 205] and defines their optical properties [204]. The molecular packing coefficient is expressed in [206] as:

$$k_p = N_A V \rho / M \quad (5)$$

where  $N_A$  is the Avogadro number,  $\rho$  is the density,  $M$  is the molecular weight,  $V$  is the intrinsic (van der Waals) volume of the molecule, calculated from the van der Waals volume increments of the individual atoms or by using the average atomic radii and chemical bond lengths.

As can be seen from table 5, the replacement of the 5,6,7,8-tetrahydroquinolin-2,6-diyl by the 1,4-phenylene, pyridin-2,5-diyl, *trans*-1,4-cyclohexylene and 1,4-bicyclo-[2.2.2]-octylene in two-fragment cyano derivatives results in a decrease of their molecular packing coefficients:



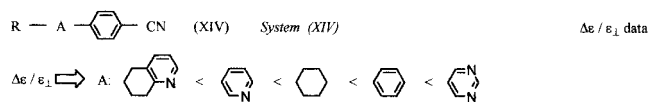
These results can be associated with the difference in the energy of intermolecular interactions (and therefore with the difference in the activation energy of the rotational viscosity of these compounds [206]).

### 6. Comparative characteristics of liquid crystals

Selection of the best components for liquid crystalline materials and the prediction of new chemical structures require comprehensive comparative investigations of the physico-chemical characteristics of liquid crystalline compounds. It has been shown that the dielectric, diamagnetic, viscous, and elastic constants, as well as the nematic-isotropic transitions of solutions of homologues, approximately obey the additive rule [207]. This fact has been employed for comparison of physico-chemical properties of liquid crystalline 2,6-disubstituted 5,6,7,8-tetrahydroquinoline cyano derivatives and other corresponding derivatives having narrow nematic ranges. This was done by using binary mixtures (containing pentyl and heptyl homologues) which give broad nematic ranges, with clearing points depending on the molecular structure in ways which are consistent with those observed for pure compounds in §2.1.1.

Table 15 shows that two-fragment 5,6,7,8-tetrahydroquinolin-2,6-diyl cyano derivatives exhibit the highest nematic thermostability in comparison with that of other corresponding derivatives. Interestingly, the introduction of the 5,6,7,8-tetrahydroquinolin-2,6-diyl into the molecular core of system (XIV) results in a decrease of

the parameter  $\Delta\epsilon/\epsilon_{\perp}$  which is favourable for supertwisted nematic display applications [197]:



### 7. Conclusions

The effects of introducing nitrogen-containing fused heterocycles into the molecular core of calamitic liquid crystals on their physico-chemical properties have been studied, and some general trends identified and explained. It is believed that this study will broaden our understanding of fundamental structure-property relationships in liquid crystals.

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