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## Liquid Crystals

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# Liquid crystalline 2,5-disubstituted pyridine derivatives

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This paper presents a review of the work on the molecular design of liquid crystalline 2,5-disubstituted pyridine derivatives for the twisted nematic (TN) and super twisted nematic (STN) liquid crystal displays (LCDs) and examines in some detail the correlations between the molecular structure of pyridine derivatives and their physico-chemical properties.

## 1. Introduction

This review is concerned with the effects of change in molecular structure on the physico-chemical properties of liquid crystals formed by 2,5-disubstituted pyridine derivatives and is aimed to provide the satisfactory selection of the best components of liquid crystal materials for TN and STN applications. For the most part, the review will be concerned with pure, single component liquid crystalline pyridines, but its scope may, where necessary, be widened to include the binary mixtures of such liquid crystals.

In the TN-LCD and STN-LCD at least ten different liquid crystal material parameters have to be optimized to achieve optimal display performance. Since a single liquid crystal shows at best one or two distinguished properties [1–33], mixtures consisting of up to twenty and more polar and weakly polar components have to be developed for a given application. The principles of the development of liquid crystal materials for TN and STN applications are briefly discussed in [34]. The review [17] is particularly helpful, and some practical examples of liquid crystal materials containing 2,5-disubstituted pyridines are presented in [5, 32].

## 2. Mesomorphic properties

When the structure, and consequently the geometry of a molecule is changed, many molecular parameters are affected and may influence in the different degrees the physico-chemical properties of liquid crystals [17, 34, 35]. The effects of structural change on the mesomorphic properties of a compound are found to be difficult to rationalize [34], therefore the purpose of this section is to define what relations can be established for

liquid crystalline 2,5-disubstituted pyridine derivatives, even though these may be empirical.

### 2.1. Effect of terminal group

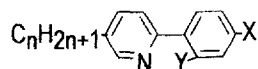
The phase transition temperatures for liquid crystalline 2,5-disubstituted pyridine derivatives are presented in tables 1–6. As can be seen from tables 1–5, 5-alkyl-2-(4-cyanophenyl)pyridines (compounds **1-1-1-5**, table 1); 2-(4-alkylphenyl)-5-cyanopyridines (compounds **2-1-2-5**, table 2); 2-cyano-5-(4-alkylphenyl)pyridines (compounds **3-1-3-4**, table 3); 2-cyano-5-(*trans*-4-alkylcyclohexyl)pyridines (compounds **4-1-4-4**, table 4); and 2-(*trans*-4-alkylcyclohexyl)-5-cyanopyridines (compounds **5-1-5-5**, table 5) show an odd–even effect in the nematic–isotropic phase transition temperatures ( $T_{N-I}$ ). Thus, the compounds with an odd number of carbon atoms in the alkyl chain have the higher values of  $T_{N-I}$  compared to compounds having an even number of carbon atoms in their alkyl chains. The same effect has been found for many other homologous series of liquid crystals and can be explained by the odd carbon atom alkyl chain having a terminal  $\text{CH}_3$  group which extends the long molecular axis, whereas in an even number carbon chain the terminal  $\text{CH}_3$  group tends to lie off axis [34]. In the corresponding alkoxy substituted series, the oxygen is equivalent to a  $\text{CH}_2$  group and a reverse situation has been found [20, 34].



It has been shown that two-ring and three-ring alkoxy substituted series of pyridine derivatives demonstrate the higher values of the melting and clearing points compared to the corresponding alkyl substituted series (compounds **1-16** and **1-17**, **2-3** and **2-6**, **2-9** and **2-10**, tables 1 and 2; see also [1, 19, 20, 26, 27]). The same effect has been found for other homologous series and can be explained by the increased conjugation and rigidity in the alkoxy substituted series [34].

The data collated in table 5 reveal that the existence of

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Table 1. Physico-chemical properties of liquid crystals [1–21]:



No.	<i>n</i>	X	Y	Mesomorphic behaviour /°C	$d_1^a/\text{Å}$	$d_2^a/\text{Å}$	$\xi_1^a/\text{Å}$	$\xi_2^a/\text{Å}$	$\varepsilon_{\perp}^b$	$\Delta\varepsilon^b$	$\mu/D$	$g^c$	$\nu^d/\text{mm}^2\text{s}^{-1}$	$\Delta n^d$	$k_p^e$
1-1	3	CN	H	Cr 43.4 N 43.8 I					9.7 <sup>f</sup>	25.3 <sup>f</sup>					0.6743
1-2	4	CN	H	Cr 32.3 N (26.5) I	13.8	19.8	50	43	13.1 <sup>f</sup>	21.4 <sup>f</sup>					0.6562
1-3	5	CN	H	Cr 33.6 N 43.5 I	15.4	22.7	42	52	10.9	17.8	6.0	0.518	50	0.214	0.6438
1-4	6	CN	H	Cr 29 N 32.5 I	16.0	25.1	38	71	12.0	15.2					0.6325
1-5	7	CN	H	Cr 30.9 N 47 I	17.9	27.2	36	83	9.2	15.8	6.15	0.495			0.6241
1-6	5	CH = CHCN	H	Cr 65.7 N 155.1 I	17.9 <sup>g</sup>	25.6 <sup>g</sup>	90 <sup>g</sup>	150 <sup>g</sup>	7.6 <sup>g</sup>	14.7 <sup>g</sup>				0.323	
1-7	5	OCF <sub>3</sub>	H	Cr 18 S <sub>B</sub> 38.5 S <sub>A</sub> 52.4 I	18.7					11.8 <sup>d</sup>				0.074	
1-8	5	OCHF <sub>2</sub>	H	Cr 26 S 43.6 I						15.9 <sup>d</sup>			12	0.125	
1-9	5	SCHF <sub>2</sub>	H	Cr 2.5 I						22.9 <sup>d</sup>			9	0.133	
1-10	5	NCS	H	Cr 34 S <sub>A</sub> 98.5 I	19.9					15.5 <sup>d</sup>			18	0.220	
1-11	5	OCF <sub>2</sub> Cl	H	Cr 36 I											
1-12	5	F	H	Cr 28.1 I						9.8 <sup>d</sup>			0.074		
1-13	5	 -CN	H	Cr 90 S 162 N 254 I						21.4 <sup>d</sup>				0.344	
1-14	6	OC <sub>6</sub> H <sub>13</sub>	H	Cr 22 S 66 N 69 I											
1-15	6	OC <sub>6</sub> H <sub>13</sub>	F	Cr 16 N 21.5 I											
1-16	5	C <sub>4</sub> H <sub>9</sub>	H	Cr 42 I											
1-17	5	OC <sub>4</sub> H <sub>9</sub>	H	Cr 60 N 65 I											
1-18	3	 -C <sub>5</sub> H <sub>11</sub>	H	Cr 113 S 121 N 225 I											

$$^a T_{\text{meas}} = T_{N-1} - 10^\circ\text{C}.$$

$$^b \tau = T_{\text{meas}}/T_{N-1}, K = 0.95.$$

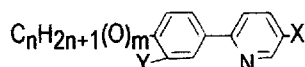
$$^c T_{\text{meas}} = T_{N-1}.$$

<sup>d,f</sup> Extrapolated values of the dielectric anisotropy  $\Delta\varepsilon$ , optical anisotropy  $\Delta n$  and kinematic viscosity  $\nu$  from the 10 % w/w solution in ZLI-1132 at 20°C and from 50 % w/w solution in 4,4'-pentylcyanobiphenyl, respectively.

$$^e T_{\text{meas}} = 40^\circ\text{C}.$$

$$^g T_{\text{meas}} = T_{N-1} - 75^\circ\text{C}.$$

Table 2. Physico-chemical properties of liquid crystals [1, 9, 16, 17, 19, 20, 22–24]:



No.	<i>n</i>	<i>m</i>	X	Y	Mesomorphic behaviour /°C	$d_1^a/\text{Å}$	$d_2^a/\text{Å}$	$\xi_1^a/\text{Å}$	$\xi_2^a/\text{Å}$	$\varepsilon_{\perp}^b$	$\Delta\varepsilon^b$	$\mu/D$	$g^c$	$k_p^d$
2-1	3	0	CN	H	Cr 58.7 N 69 I	13.6	23.5	65	59	8.9	9.4			
2-2	4	0	CN	H	Cr 39.3 N 55 I									
2-3	5	0	CN	H	Cr 47.4 N 68 I	15.4	26.0	45	66	8.0	6.5	4.48	0.537	0.6631
2-4	6	0	CN	H	Cr 42.2 S 51.7 N 62.3 I	16.5	27.3	40	135	7.8	4.8			
2-5	7	0	CN	H	Cr 47.2 S 66.8 N 70.3 I	18.4 <sup>e</sup>	29.6 <sup>e</sup>	38 <sup>e</sup>	150 <sup>e</sup>	7.7	3.1			
2-6	5	1	CN	H	Cr 59.3 N 94.6 I									
2-7	1	1	C <sub>6</sub> H <sub>13</sub>	H	Cr 57 I									
2-8	1	1	C <sub>6</sub> H <sub>13</sub>	F	Cr 53.7 I									
2-9	5	0	C <sub>4</sub> H <sub>9</sub>	H	Cr 17.4 N 21.8 I									
2-10	5	0	OC <sub>4</sub> H <sub>9</sub>	H	Cr 38 S (34) I									

$$^a T_{\text{meas}} = T_{N-1} - 10^\circ\text{C}.$$

$$^b \tau = T_{\text{meas}}/T_{N-1}, K = 0.95.$$

$$^c T_{\text{meas}} = T_{N-1}.$$

$$^d T_{\text{meas}} = 40^\circ\text{C}.$$

$$^e T_{\text{meas}} = T_{N-1} - 5^\circ\text{C}.$$

Table 3. Physico-chemical properties of liquid crystals [3, 5, 7, 9, 13, 16, 17, 24–29]:

$$C_nH_{2n+1}-(\text{C}_6\text{H}_{10})_k-\text{C}_6\text{H}_4-\text{C}_5\text{H}_3\text{N}(\text{X})(\text{Y})$$

No.	<i>n</i>	<i>k</i>	X	Y	Mesomorphic behaviour/°C	$\Delta\varepsilon^a$	$\mu/D$	$g^b$	$\Delta n^a$	$v^a/\text{mm}^2\text{s}^{-1}$	$k_p^c$
3-1	4	0	CN	H	C 64 I						
3-2	5	0	CN	H	C 73 N (38.5) I	17.9	6	0.466	0.204		0.6656
3-3	6	0	CN	H	C 58 N (44) I						
3-4	7	0	CN	H	C 66 N (56) I						
3-5 <sup>e</sup>	5	0		H	C 76 N 232.1 I	16.7 <sup>d</sup>			0.344	115	
3-6	5	0		H	C 150 S (126) I	8.3			0.179		
3-7	5	0		H	C 136 S 168.5 N 310 I	17.6			0.404		
3-8	6	0		H	C 72 S 166 N 221 I						
3-9	6	0		H	C 62 N 93 I						
3-10	5	1	F	F	C 58 N 107 I						
3-11	3	0		H	C 58 S <sub>B</sub> 124 S <sub>A</sub> 134 N 156 I						
3-12	5	1	C <sub>3</sub> H <sub>7</sub>	F	C 64 S <sub>A</sub> (63) N 122 I						

<sup>a</sup> Extrapolated values from the 10% w/w solution in ZLI-1132 at 20°C.

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

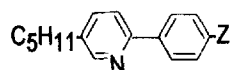
<sup>c</sup>  $T_{\text{meas}} = 40^\circ\text{C}$ .

<sup>d</sup>  $\tau = T_{\text{meas}}/T_{N-1}$ ,  $K = 0.70$ , the direct measurement.

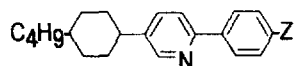
<sup>e</sup>  $d_1 = 20.5 \text{ \AA}$ ,  $d_2 = 27 \text{ \AA}$ ,  $\xi_1 = 100 \text{ \AA}$ ,  $\xi_2 = 130 \text{ \AA}$ ,  $T_{\text{meas}} = T_{N-1} - 100^\circ\text{C}$ .

a double bond and its position in the structure of alkenyl chain strongly affect the mesomorphic behaviour of 2,5-disubstituted pyridines (compounds 5-8 and 5-14, 5-13 and 5-15; see also [3, 32, 36].

As can be seen from tables 1, 4 and [3–6], the clearing points for liquid crystals of general formulas:



grow depending on Z as follows:  $\text{SCHF}_2 < \text{OCF}_2\text{Cl} < \text{F} < \text{CN} \approx \text{OCHF}_2 < \text{OCF}_3 < \text{NCS}$



grow depending on Z as follows:  $\text{OCF}_2\text{Cl} < \text{OCF}_3 < \text{OCHF}_2 < \text{CN}$ . This reveals that the polar group efficiency can be different for two-ring and three-ring pyridine derivatives.

## 2.2. Effect of rigid core structure

The introduction of a pyridin-2,5-diyl group into

molecular structure leads to the great diversity of mesomorphic properties of liquid crystals depending on its position in the molecular rigid core and on the position of a nitrogen atom in the pyridin-2,5-diyl group [1–33, 37]. Thus, the relationship between the clearing points and the nematic ranges and rigid core structure for two-ring (A–B) or three (A–B–C) liquid crystalline 2,5-disubstituted pyridine derivatives and other well-known derivatives can be expressed by the following orders of increasing clearing points and nematic ranges (for three-ring compounds) (see tables 1–6 and [1–5, 8, 18–20, 23–33, 36, 38–65]): for liquid crystals of the following general formulas, the clearing points, depending on the structure of the rigid core (A–B), grow as follows:

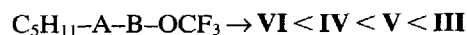
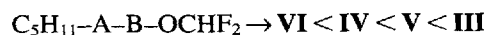
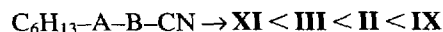
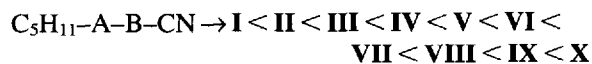
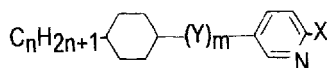
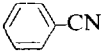
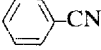
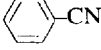
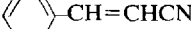
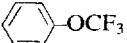
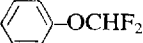
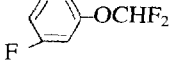
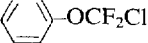




Table 4. Physico-chemical properties of liquid crystals [3–5, 9–10, 14, 16–18, 30]:



No.	<i>n</i>	<i>X</i>	<i>Y</i>	<i>m</i>	Mesomorphic behaviour/ $^{\circ}\text{C}$	$d_2^a/\text{\AA}$	$\xi_2^a/\text{\AA}$	$\varepsilon_{\perp}^b$	$\Delta\varepsilon^b$	$\mu/\text{D}$	$g^d$	$\Delta n^e$
4-1	4	CN		0	Cr 60.7 N (37) I							
4-2 <sup>f</sup>	5	CN		0	Cr 45.4 N 55.4 I	24.8	60	10.8	12.1	5.84	0.615	0.084
4-3	6	CN		0	Cr 35.3 N 49.4 I	26.4	75	11.0	11.5			0.0837
4-4	7	CN		0	Cr 50.1 N 60.2 I	28.5	88	9.5	10.3			0.083
4-5	5	CN	C <sub>2</sub> H <sub>4</sub>	1	Cr 86.5 N (53) I				16.2 <sup>g</sup>			0.115 <sup>g</sup>
4-6	3			0	Cr 123 N 237 I							
4-7	4			0	Cr 124 N 228 I							
4-8	5			0	Cr 113 N 228 I			3.2 <sup>c</sup>	14 <sup>c</sup>			0.232 <sup>g</sup>
4-9	3			0	Cr 133 N 318.4 I							
4-10	4			0	Cr 35.1 S 149.2 N 154.8 I				10.6 <sup>g</sup>			0.123 <sup>g</sup>
4-11	4			0	Cr 57.1 S 135.7 N 165.3 I				13.8 <sup>g</sup>			0.154 <sup>g</sup>
4-12	4			0	Cr 39.6 S 78.3 N 136.4 I							
4-13	4			0	Cr 79.5 S 121.7 N 130.3 I				12.2 <sup>g</sup>			0.134 <sup>g</sup>
4-14	3			0	Cr 99 N 157.3 I							
4-15	3			0	Cr 59.1 N 109 I							

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

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

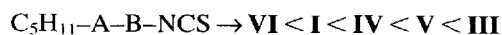
<sup>c</sup>  $\tau = 0.75$ .

<sup>d</sup>  $T_{\text{meas}} = T_{N-I}$ .

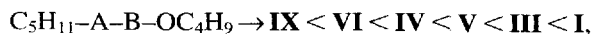
<sup>e</sup>  $\tau = 0.99$  (compound 4-2), 0.98 (compounds 4-3 and 4-4).

<sup>f</sup>  $k_p = 0.6353$  at  $40^{\circ}\text{C}$ ,  $\nu = 41 \text{ mm}^2 \text{ s}^{-1}$  at  $20^{\circ}\text{C}$ .

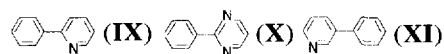
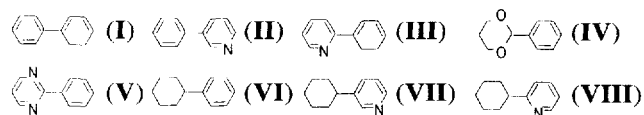
<sup>g</sup> Extrapolated values from the 10% w/w solution in ZLI-1132 at  $20^{\circ}\text{C}$ .



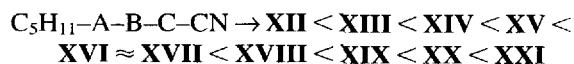
(the clearing points and the nematic ranges)



where A–B are the following structures:



For liquid crystals of the following general formulas, the clearing points and the nematic ranges, depending on the structure of the rigid core (A–B–C), grow as follows:



(clearing points),

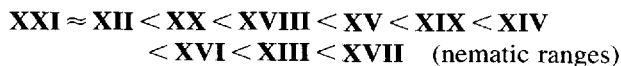
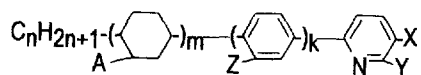


Table 5. Physico-chemical properties of liquid crystals [3, 5, 10, 14, 16–17, 29, 31–33]:



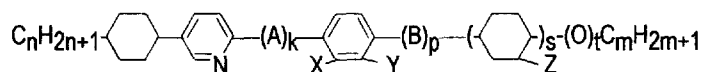
No.	<i>n</i>	<i>X</i>	<i>m</i>	<i>Y</i>	<i>Z</i>	<i>k</i>	<i>A</i>	Mesomorphic behaviour/ <sup>o</sup> C	<i>d</i> <sub>2</sub> <sup>a</sup> /Å	$\xi_2^a$ /Å	$\epsilon_{\perp}^b$	$\Delta\epsilon^b$	$\mu/D$	<i>g</i> <sup>c</sup>	<i>k</i> <sub>p</sub> 40 <sup>o</sup> C
5-1	3	CN	1	H		0	H	Cr 48 N 53.6 I	24.0	63	7.4	4.3			
5-2	4	CN	1	H		0	H	Cr 32 N 49.2 I							
5-3	5	CN	1	H		0	H	Cr 48 N 64.2 I							
5-4	6	CN	1	H		0	H	Cr 36.3 S 41.4 N 60.4 I	27.3	74	6.5	3.7	4.03	0.676	0.6381
5-5	7	CN	1	H		0	H	Cr 47.6 S 52.2 N 66.2 I	29.5	97	6.9	2.9			
5-6	3	CN	2	H		0	H	Cr 88.5 S 102.7 N 245.2 I	30.8	115	6.8	2.3			
5-7	3	CN	2	Cl		0	H	Cr 105.3 N 124.8							
5-8	5	C <sub>3</sub> H <sub>7</sub>	1	H	H	1	H	Cr 37 S 94 N 179 I							
5-9	5	C <sub>3</sub> H <sub>7</sub>	1	H	F	1	H	Cr 66 N 151 I							
5-10	3	C <sub>2</sub> H <sub>5</sub>	1	H	H	1	H	Cr 50.8 S 87.7 N 174.4 I	{19.5}	{46}					
5-11	3	C <sub>2</sub> H <sub>5</sub>	1	H	NH <sub>2</sub>	1	H	Cr 86 N 127 I	{21.7}	{110}					
5-12	3	C <sub>2</sub> H <sub>5</sub>	1	H	F	1	H	Cr 60.2 N 145 I	{19.7}	{38}					
5-13	5	C <sub>3</sub> H <sub>7</sub>	1	H	H	1	CH <sub>3</sub>	Cr 15 N 111 I							
5-14	5	CH <sub>2</sub> -CH=CH <sub>2</sub>	1	H	H	1	H	Cr 68.7 S 107.8 N 163.6 I							
5-15	5	CH <sub>2</sub> -CH=CH <sub>2</sub>	1	H	H	1	CH <sub>3</sub>	Cr 53 N 83.2 I							
5-16	5	C <sub>3</sub> H <sub>7</sub>	1	F	H	1	H	Cr 60 S 91 S <sub>A</sub> 124 N 150 I							
5-17	3	CN	1	H	H	1	H	Cr 117 N 252 I							
5-18	3	CN	1	Cl	H	1	H	Cr 109.4 N 120.7 I							

<sup>a</sup>  $T_{\text{meas}} = T_{N-1} - 10^{\circ}\text{C}$ ,  $\{d_1, \xi_1, T_{\text{meas}} = T_{N-1} - 40^{\circ}\text{C}\}$ .

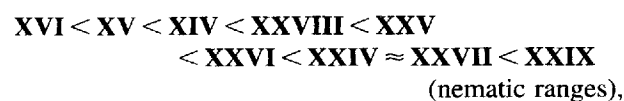
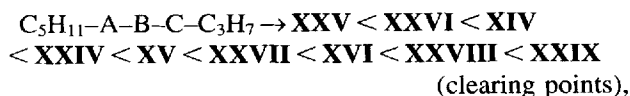
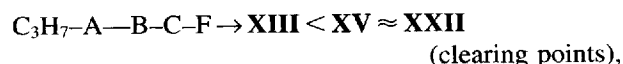
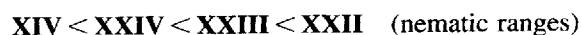
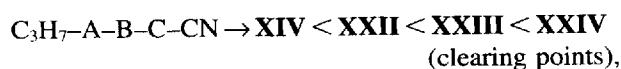
<sup>b</sup>  $\tau = T_{\text{meas}}/T_{N-1}$ ,  $K = 0.95$ .

<sup>c</sup>  $T_{\text{meas}} = T_{N-1}$ .

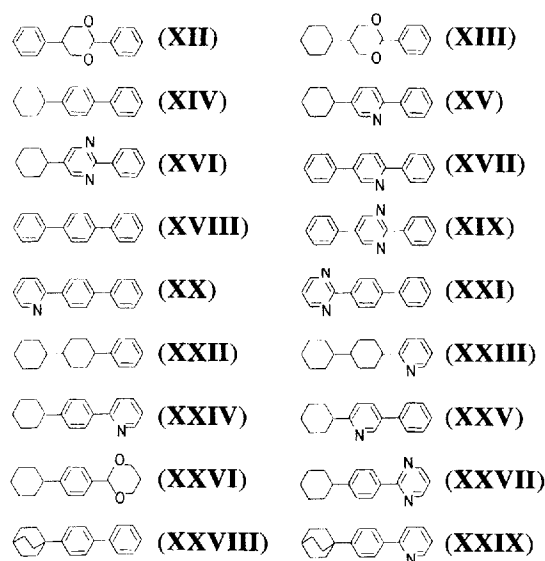
Table 6. Mesomorphic properties of liquid crystals:



No.	<i>n</i>	<i>m</i>	<i>t</i>	<i>A</i>	<i>k</i>	<i>B</i>	<i>p</i>	<i>s</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	Mesomorphic behaviour/ <sup>o</sup> C	Reference
6-1	5	3	0		0		0	0	H	H	H	Cr 48 S <sub>B</sub> 163 S <sub>A</sub> 184 N 185 I	[28]
6-2	2	5	0		0		0	0	H	H	H	Cr 38 S 138 N 156 I	[8]
6-3	2	5	0		0		0	0	H	NO <sub>2</sub>	H	Cr 30 N 42 I	[5]
6-4	2	5	0		0		0	0	H	NH <sub>2</sub>	H	Cr 63.1 N 120 I	[5]
6-5	2	5	0		0		0	0	H	F	H	S 120 N 127 I	[5]
6-6	4	1	1		0		0	0	H	H	H	Cr 87 S 142 N 208.2 I	[8]
6-7	4	1	1		0		0	0	H	F	H	Cr 94 S 138.8 N 179.8 I	[5]
6-8	4	1	1		0		0	0	F	H	H	Cr 45.2 N 174.5 I	[6]
6-9	2	4	1	C <sub>2</sub> H <sub>4</sub>	1		0	0	H	H	H	Cr 48 S 61 N 93 I	[32]
6-10	2	4	1	C <sub>2</sub> H <sub>2</sub>	1		0	0	H	H	H	Cr 90 S 114 N 230 I	[32]
6-11	2	4	1	C≡C	1		0	0	H	H	H	Cr 130 N 207 I	[32]
6-12	3	5	0		0		0	0	H	H	H	Cr 30 S 173 N 181 I	[8]
6-13	3	5	0		0		0	0	F	H	H	Cr 47 N 149 I	[28]
6-14	2	5	0		0		0	1	H	H	H	Cr 50 S 200 N 299 I	[5]
6-15	2	5	0		0		0	1	H	H	CH <sub>3</sub>	Cr 70 S 145 N 248 I	[32]
6-16	2	5	0		0		0	1	H	NO <sub>2</sub>	H	Cr 87 N 168 I	[5]
6-17	2	5	0		0		0	1	H	NH <sub>2</sub>	H	Cr 98.1 S 135 N 212.4 I	[5]
6-18	2	5	0		0		0	1	H	F	H	Cr 104.6 N 270 I	[5]
6-19	2	3	0	C <sub>2</sub> H <sub>4</sub>	1		0	1	H	H	H	Cr 140 N 196 I	[32]
6-20	2	3	0		0	C <sub>2</sub> H <sub>4</sub>	1	1	H	H	H	Cr 99 S 161 N 262 I	[32]



where A–B–C are the following structures:



The presented orders of increasing clearing points and nematic ranges for the liquid crystals of given general formulas reveal that the polar and weakly polar compounds with the same rigid core can have different relationships with their mesomorphic properties; and liquid crystalline 2,5-disubstituted pyridine derivatives show approximately the same relationship between molecular structure and their mesomorphic properties as well-known 2,5-disubstituted pyrimidine derivatives compared only compounds with the same substituents and with the same position of the pyridin-2,5-diyl and pyrimidin-2,5-diyl groups, respectively.

The effects of the introduction of the pyrimidin-2,5-diyl and *trans*-1,3-dioxan-2,5-diyl groups into molecular structure of 2,5-disubstituted pyridines were demonstrated in [66, 67].

As can be seen from tables 4 and 6 and [3, 68–72], the effect of introducing different linking groups into the molecular structure of liquid crystals is most marked in the

case of three- and four-ring compounds; thus, the position of  $-CH_2-CH_2-$ ,  $-C\equiv C-$  and  $-CH=CH-$  linking groups in the rigid core of liquid crystalline 2,5-disubstituted pyridine derivatives have considerable opposite effects on the mesomorphic behaviour of these liquid crystals. So far the  $-CH_2-CH_2-$  linking group, that increases the molecular flexibility which in turn leads to effective broadening of the molecule and reduction in intermolecular attractive force effects, can decrease the melting and clearing points of the pyridine derivatives [5, 19, 28, 32, 36, 73, 74]; while the  $-C\equiv C-$  and  $-CH=CH-$  linking groups, that increase the conjugation length of  $\pi$ -electrons and, therefore, enhance molecular polarizability, increase the nematic thermostability (see, for example, compounds 1-3 and 1-6, 3-5 and 3-7, 4-6 and 4-9, tables 1, 3 and 4; see also [3, 5, 32, 61, 65]). The same effects have been found for many other liquid crystalline derivatives [34].

The effects of the introduction of COO and  $CH_2O$  linking groups into the molecular structure of 2,5-disubstituted pyridines on their mesomorphic behaviour have been shown in [29, 74–76] and [29, 74], respectively.

The data collated in tables 1–6 and [4–6, 18, 27–30, 32, 33, 77] reveal that the lateral F, Cl,  $NO_2$ ,  $NH_2$ ,  $CH_3$  substitutions have a considerable effect on the mesomorphic properties of the pyridine derivatives resulting in reducing the smectic and nematic thermostabilities due to the lateral substituents broadening the molecule and reducing intermolecular forces (compounds 1-14 and 1-15; 2-7 and 2-8; 3-8 and 3-9; 3-10, 3-12; 4-11 and 4-12; 4-14 and 4-15; 5-6 and 5-7; 5-8 and 5-9, 5-13, 5-16; 5-10 and 5-11, 5-12; 5-14 and 5-15; 5-17 and 5-18; 6-2 and 6-3, 6-4, 6-5; 6-6 and 6-7, 6-8; 6-12 and 6-13; 6-14 and 6-15–6-18). The same effects have been found for other liquid crystalline derivatives [34].

It has been reported that the lateral hydroxy substituted pyridine derivatives exhibit higher melting and clearing points compared to the corresponding unsubstituted compounds [20, 32, 77]. This may well be due to the enhanced axial molecular polarizability resulting from delocalization of  $\pi$ -electrons caused by intramolecular hydrogen bonding.

### 3. X-ray diffraction study of 2,5-disubstituted pyridines

The investigation of polar liquid crystals by X-ray 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  $d > L$ , and in some cases, the simultaneous existence of two fluctuation layer structures with incommensurate periods  $d_1$  and  $d_2$ , where  $d_1 < L$  and  $L < d_2 < 2L$ , where  $L$  is the molecular length [7, 9, 10, 12, 22].

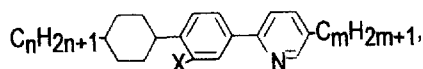
It has been shown that  $d_1$  and  $d_2$  increase with the length

of the alkyl chain for 4 series of two-ring pyridine cyano derivatives as a result of the increased size of the molecule and of its dimer (see tables 1, 2, 4 and 5 and [10, 22]). The correlation length  $\xi_2$  also increases, whereas  $\xi_1$  decreases. Thus, the smectic-like fluctuations on the dimeric density wave are predominant in the homologues with a long alkyl chain, whereas in the homologues with a short alkyl chain the smectic-like fluctuations on the dimeric and monomeric density waves have comparable intensities, and in the molecule with a propyl radical the monomeric density wave could predominate over the dimeric one (compounds 1-2-1-5, 2-1, 2-3-2-5; tables 1 and 2, [10, 22]).

From tables 2, 4 and 5 follows that the presence of the *trans*-1,4-cyclohexylene group in the molecular rigid core of two-ring pyridine cyano derivatives is unfavourable for the generation of smectic-like fluctuations on the monomeric density wave (compounds 2-3 and 5-3, 4-2) [7, 9, 10, 12]. Comparison of the properties of compounds 1-3 and 1-6 shows that the replacement of the CN end group by the longer polar CH=CH-CN end group does not alter the structure of the nematic phase, see table 1 and [7, 9, 10, 12]. The same effects were found for *trans*-4-alkyl-(4'-cyanophenyl)cyclohexanes [9, 12].

Recent X-ray investigations have demonstrated that for liquid crystalline pyridine derivatives incorporating OCF<sub>3</sub> and NCS end groups only the monomer layer structure with the period  $d_1$  was found (compounds 1-7, 1-10, table 1) [21]. It has been reported that the rate at which  $\xi_2$  increases with decreasing temperature increases with the length of the alkyl chain, indicating highly smectogenic properties in the higher homologues of 2-cyano-5-(*trans*-4-alkylcyclohexyl)pyridines [10]. The smectogenicity of the homologous series, defined by  $\xi_2$  values, increases in sequence: 5-alkyl-2-(4-cyanophenyl)pyridines, 2-cyano-5-(*trans*-4-alkylcyclohexyl)pyridines, 2-(*trans*-4-alkylcyclohexyl)-5-cyanopyridines, 2-(4-alkylphenyl)-5-cyanopyridines (tables 1, 2, 4 and 5, and [10]).

For weakly polar compounds of general formula:



where  $X = \text{H}, \text{NH}_2, \text{F}$ ; only the monomeric density wave was observed with a characteristic period  $d_1$  (compounds 5-10-5-12, table 5, and [10, 12]). For three pairs of compounds having molecules of identical length ( $X = \text{H}$ ), it has been found that the larger  $\xi$  value belongs to the compound in which the longer radical is attached to the pyridine ring ( $n < m$ ) [10]. For three pairs of compounds ( $X = \text{H}$ ) in which the radical on the cyclohexane ring is unchanged and the radical on the pyridine ring increases, it has been found that  $\xi$  increases with increasing length of the radical [10]. A somewhat unusual situation has been

observed for compound 5-11. The length of its molecules agrees with that for 5-10 and 5-12, but  $d_1$  is appreciably greater. Presumably, due to the interaction with a neighbouring molecule (taking into account the attraction and the steric factors), the presence of the lateral substituent  $\text{NH}_2$  leads to a fluctuation layered structure, whose period is greater than the length of an individual molecule as a result of a longitudinal shift of neighbouring molecules relative to one another. Compound 5-11 is the most smectogenic (highest value of  $\xi_1$ ) and compound 5-12 with a fluorine atom as a lateral substituent is the least smectogenic (as expected) among the weakly polar compounds 5-10-5-12 examined, table 5 and [10, 12].

Since the increase in the correlation lengths potentially suggests smectogenic properties in the liquid crystal (LC), these results allow a rational selection of components for the liquid crystal materials with a controlled ratio of smectic to nematic phases.

#### 4. 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  $\mathbf{n}$ ; is described by the theory of Maier and Meier [78]:

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

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 (as well as optical and elastic) properties of liquid crystals with the different nematic-isotropic (N-I) transition temperatures  $T_{N-I}$  can only be made at constant reduced temperature  $\tau = T/T_{N-I}$  [79].

Tables 1-4 and 7 present some data on the dielectric properties of liquid crystalline pyridines measured at a constant reduced temperature and extrapolated from the liquid crystal mixture at 20°C. According to [79], the extrapolations are not meaningful, however these estimations are only one way to obtain a rough definition of the dielectric (as well as optical and elastic) properties of non-mesomorphic components of liquid crystal materials, smectic liquid crystals, and LCs with narrow nematic range.

As can be seen from tables 1-5 and 7 the introduction of the pyridin-2,5-diyl group into the LC compound structure results in a great diversity of dielectric properties because the position of the nitrogen atom and the related dipole moment of the pyridin-2,5-diyl group considerably



Table 7. Physico-chemical and electro-optical ( $d$ -cell gap = 10  $\mu$ ,  $u = 3$  v) properties of binary mixtures ( $C_5$  and  $C_7 = 40$  % mol: 60 % mol) of the liquid crystals [3, 9, 17, 37].

No.	Formula	$T_{N-1}/^{\circ}\text{C}$	$d_2^a/\text{\AA}$	$\xi_2^a/\text{\AA}$	$\gamma_1^b/P$	$E^b/\text{eV}$	$\frac{K_3^c}{K_1}$	$\varepsilon_{\perp}^c$	$\Delta\varepsilon^c$	$\frac{\Delta\varepsilon^c}{\varepsilon_{\perp}}$	$\Delta n^c$	$U_{90}^b/\text{V}$	$U_{10}^b/\text{V}$	$\tau_{\text{on}}^i/\text{ms}$	$\tau^{2b}/\text{ms}$	$\tau_{\text{off}}^b/\text{ms}$
1		44.1	25.6	63	1.84	0.54	1.25	10.7	16	1.5	0.175	1.08	1.54	75	20	105
2		69.1	27.9	250	3.50	0.505	1.11	8.7	7.3	0.85	0.172	1.90	2.63	130 <sup>d</sup>	30 <sup>d</sup>	60 <sup>d</sup>
3		49.0	26.6	117	2.20	0.495	1.31	11.3	11.3	1.0	0.175	1.53	2.16	130	30	105
4		57.7	27.0	69	1.78	0.480	1.53	10.0	12.4	1.24	0.093	1.25	1.82	114	30	95
5		51.0	23.0	50	1.90	0.565	1.06	8.7	19.6	2.86	0.174	1.07	1.48	70	20	90
6		56.4	28.5	62	1.00	0.410	1.68	5.4	9.2	1.71	0.100	1.67	2.32	133	33	46
7		39.0	27.4		1.10	0.546	1.37	6.0	11.7	1.95	0.184	1.30	1.78	85	21	69
8		106	27.8	342			1.93									
9		64.3			1.40	0.485	1.37	7.5	3.3	0.44	0.104	2.50	3.45	130 <sup>d</sup>	20 <sup>d</sup>	43 <sup>d</sup>

<sup>a</sup>  $T_{\text{meas}} = T_{N-1} - 10^{\circ}\text{C}$ .<sup>b</sup>  $T_{\text{meas}} = 25^{\circ}\text{C}$ .<sup>c</sup>  $T_{\text{meas}}/T_{N-1}$ ,  $K = 0.95$ .<sup>d</sup>  $U = 5$  V.

affect the magnitude and the direction of the total dipole moment; for example, when the longitudinal component of the dipole moment for the pyridin-2,5-diyl group coincides with that for the CN group,  $\Delta\varepsilon$  grows (compounds 1-1-1-5, 3-2, 4-2-4-4; mixtures 1, 3, 4; tables 1, 3, 4 and 7 and [2, 3, 13, 14, 37]), in the other case  $\Delta\varepsilon$  decreases (compounds 2-1, 2-3-2-5, 5-1, 5-3-5-5; mixtures 2, 9; tables 2, 5 and 7 [2, 3, 13, 14, 37]). Tables 1, 2, 4 and 5 present the data showing an odd-even effect in the dielectric properties of two-ring pyridine cyano derivatives [2, 3]. As can be seen from tables 1-5 and 7, for definite chemical structure of liquid crystals, the dielectric anisotropy  $\Delta\varepsilon$  decreases approximately in the same sequence as the values of dipole moments for terminal groups [3, 16, 17]: CN, NCS, OCHF<sub>2</sub>, OCF<sub>3</sub>, F diminish in the order 4.05, 3.59, 2.46, 2.36, 1.47, respectively.

It has been shown that mesogenic molecules possessing strongly polar end groups form associated pairs. Both head-to-head and head-to-tail pairing occurs [80-82], but

anti-parallel association predominates and reduces the effective dipole moment [83]:

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

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

where  $\varepsilon_i^{\infty} = 1.05n_i^2$ ;  $g$  is the correlation factor [83].

The results presented in tables 1-5 reveal the relationship between  $g$  and liquid crystalline molecular structures of 2,5-disubstituted pyridine derivatives. Thus, the position of the nitrogen atom in the pyridin-2,5-diyl group as well as the introduction of the *trans*-1,4-cyclohexylene fragment into the molecular structure of two-ring pyridine cyano derivatives strongly affects the correlation factor leading, in the last case, to it increasing (compounds 2-3 and 5-3, 3-2 and 4-2, tables 2-5) [16]. The same effects were found for the *trans*-4-alkyl-(4'-cyano-phenyl)cyclohexanes and for the *trans*-4-alkyl-(4'-cyano-cyclohexyl)cyclohexanes [83].

### 5. Optical properties

The phenomenological relation between the refractive index and the electric polarization can be defined as [84, 85]:

$$(n^{*2} - 1)/(n^{*2} + 2) = N\alpha^*/3\epsilon_0, \quad (4)$$

where the mean polarizability  $\alpha^* = (\alpha_{\parallel} + 2\alpha_{\perp})/3$ ;  $n^{*2} = (n_c^2 + 2n_o^2)/3$ ;  $n_o$  is the ordinary and  $n_e$  is the extraordinary refractive indices. From equation (4) and the previous section, it follows that the aromatic compounds which have large induced polarizability of their highly conjugated  $\pi$ -electron system exhibit the optical anisotropy  $\Delta n = n_e - n_o$  that is much larger than that of non-aromatic compounds (tables 1–5 and 7 and [2–4, 13–15, 17, 18, 37]).

It has been found that liquid crystalline pyridines incorporating the *trans*-1,4-cyclohexylene group or/and halogen substituted end groups exhibit lower values of the optical anisotropy compared to the corresponding compounds having the 1,4-phenylene group or/and cyano end group (compounds 1-3 and 1-12, 3-2 and 4-2, 3-5 and 3-6, 4-8 and 4-10, 4-11, 4-13; mixtures 2 and 9, 3 and 4; tables 1, 3, 4 and 7, see also [2–4, 13–15, 17, 18]). These can be explained in terms of reducing the effective conjugation length of the  $\pi$ -electron system resulting in a shorter resonance wavelength of UV absorption spectrum for the liquid crystals incorporating the *trans*-1,4-cyclohexylene group or/and halogen substituted end groups than for corresponding compounds incorporating the 1,4-phenylene group or/and CN end group [86–88].

### 6. Viscoelastic properties

It has been shown that liquid crystal materials for TN and STN applications should have a low viscosity to give acceptable response times for LCDs [89, 90]. According to the theoretical predictions and the results on the kinematic viscosity  $\nu$  and rotational viscosity  $\gamma_1$  presented in tables 1–5 and 7, viscosity is minimized in the molecular structures of 2,5-disubstituted pyridine derivatives of minimal polarity and polarizability, with short terminal groups and lacking lateral substituents.

The elastic constant ratio  $K_3/K_1$  is the parameter of the great importance for STN-LCDs defining their electro-optical performance [91]. It has been shown that elastic constant ratio  $K_3/K_1$  is a linear function of the squared dimeric density wave period  $d_2^2$  for the binary mixtures of two-ring pyridine cyano derivatives and other cyano derivatives presented in table 7 [9]. This can be explained by using the following expression (5) [92].

$$\frac{K_3}{K_1} = \frac{4L^2}{3W^2} \times \frac{\langle be(\alpha) \rangle}{\langle st(\alpha)\rho^2 \rangle}, \quad (5)$$

where  $L$  and  $W$  represent the length and width of a liquid crystalline molecule, respectively, and factors  $\langle be(\alpha) \rangle$  and

$\langle st(\alpha)\rho^2 \rangle$  characterize the degree of short range smectic-like ordering and can be correlated with the measured values of the longitudinal and transverse correlation lengths [93]. Initially, in order to simplify the analysis, concentration on purely geometrical factors as of major importance, in which case:

$$K_3/K_1 \sim L^2/W^2. \quad (6)$$

Taking  $W^d$  as the effective width of the cyano derivative dimer (in first approximation the same for all cases studied),  $L^d$  as effective length of the dimer (proportional to  $d_2$ ), equation (6) describes the experimental situation correctly [9]. In this interpretation the dimers formed by the cyano derivatives play an important role. In combination with the better development of the dimeric density wave as compared to the monomeric one, this proves that for fifth and older homologues of two-ring pyridine cyano derivatives and other cyano derivatives the balance in the monomer–dimer system  $2M \rightleftharpoons D$  (considering data on the correlation factor in tables 1–5 and on the correlation lengths in tables 1, 2, 4 and 5) is biased towards dimers defining the liquid crystal properties [9, 16, 17].

It has been reported that for liquid crystalline two-ring pyridine derivatives incorporating NCS and OCF<sub>3</sub> end groups only the monomer layer structure with period  $d_1$  was found (§ 3 and [21]). This leads to the possible suggestion that the liquid crystalline properties of pyridine derivatives with NCS or with halogen substituted end groups are determined by their monomers. This model can be used in the interpretation of their lower values of the viscosity than that of the corresponding cyano derivatives (compounds 1-3 and 1-8–1-10, table 1 and [3, 4]).

### 7. Molecular packing

It has been shown that LC molecular packing plays a very important role in the creation of the mesophases [94]. Tables 1–5 present the values of the molecular packing coefficient  $k_p$  for the homologous series of 5-alkyl-2-(4-cyanophenyl)pyridines and for the fifth homologues of other series [11, 17]. Molecular packing coefficient is defined as [11]:

$$k_p = N_A V \rho / M, \quad (7)$$

where  $N_A$  is the Avogadro number,  $\rho$  is the density,  $M$  is the molecular weight,  $V$  is 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. It is clear from table 1 that increasing the length of the alkyl chain lowers the molecular packing coefficient (as expected, compounds 1-1–1-5) [11]. The observed difference in  $k_p$  for the compounds presented in tables 1–5 can be associated with the difference in the energy of intermolecular interactions (and therefore with the difference in the

activation energy  $E$  of the rotational viscosity  $\gamma_1$  observed for these compounds in table 7 [3, 37]).

### 8. Comparative characteristics of liquid crystals

Selection of the best components for the liquid crystal materials and prediction of new chemical structures need comprehensive comparative investigations of physico-chemical and electro-optical 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 [95]. This fact is employed for the comparison of physico-chemical and electro-optical properties of liquid crystalline pyridines and other liquid crystals having narrow nematic ranges by using binary mixtures (containing a pentyl and a heptyl homologue) which give broad nematic ranges. Table 7 shows that by choosing a particular structure of pyridine cyano derivatives the physico-chemical properties can be varied over a wide range and a desired set of electro-optical parameters can be obtained.

### 9. Conclusions

From the design of specific molecular structures and from investigations into physico-chemical and electro-optical properties we have shown that a wide range of material parameters results in the liquid crystalline 2,5-disubstituted pyridine derivatives which are of real use for TN and STN applications.

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