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Alkoxylation in achiral calamitic liquid crystals

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This review examines in some detail the effect on physico-chemical and electro-optical properties of introducing alkoxy groups into the molecular structure of achiral calamitic liquid crystals. The results of this study are compared with those obtained for the corresponding compounds having alkyl and other groups, and are rationalized in terms of existent theories.

1. Introduction

Liquid crystal displays (LCDs) have become, in recent decades, the most significant and fastest growing type of display technology. The operation efficiency of LCDs is essentially determined by the liquid crystalline material properties. Since these properties of liquid crystals are the result of their molecular properties amplified by long range molecular interactions, the proper application design of liquid crystalline molecules is crucial.

This review considers the characteristic substituent effects that underline the physico-chemical and electro-optical properties of achiral calamitic liquid crystals (LCs) containing terminal, linking and lateral alkoxy groups; especially those important to the development of commercial liquid crystalline materials for display applications. When possible, the physico-chemical and electro-optical properties of achiral calamitic LCs having alkoxy substituents will be compared with those of the corresponding compounds with alkyl and other well-known groups.

Many of the characteristic effects of alkoxylation can be correlated with the geometric and electronic structure of alkoxy groups. The C–O bond angle (111°) is almost the same as that of the C–C bond (112°) [1]. It has been shown that alkoxy groups exhibit electron attraction due to the induction effect ($-I$), and they can release electrons because of the conjugative effect ($+T$) [2]. The $-I$ effect of alkoxy groups is caused by the difference in the electronegativities of oxygen and carbon. It leads to the displacement of the electrical centre of gravity of the C–O valency electrons toward the oxygen atom and the resulting dipole induces partial positive charges over the rest of the molecule [2]. The $+T$ effect of alkoxy groups follows from the tendency of the unshared electrons to enhance the covalency of the oxygen atom. The resulting electron displacement can be relayed to other parts of the molecule by conjugation. These dis-

placements happen to that extent which results in the minimum energy for the system. Due to easy polarization of the unshared electrons, the presence of electron-attracting, or the highly polarizable centres in other molecular parts, will increase conjugative electron release [2]. As expected, these features of alkoxy groups introduced into the molecular structure of 1,4-phenylene, *trans*-1,4-cyclohexylene, pyridine-2,5-diyl and other derivatives facilitate the formation of the mesophases.

In the last decades, the design and synthesis of LCs containing terminal, linking and lateral alkoxy groups have attracted much interest because of the promising physico-chemical and electro-optical properties which make some of them very useful for display applications [3–13]. In this paper, the effect of terminal, linking and lateral alkoxylation on the properties of achiral calamitic liquid crystals are discussed, rationalized in terms of existing theories, and a comparison made with the corresponding alkyl and other well-known substituents.

2. Mesomorphic properties

Many attempts have been made to understand the influence of factors such as rigidity, linearity, size and polarizability of terminal, linking and lateral groups on mesophase stability [14–20]. However, the prediction and rationalization of mesomorphic properties still remain difficult problems [14–16, 21–32]. The aim of this section is therefore to define the relations that can be established for LCs having terminal, linking and lateral alkoxy groups, even though these may be empirical. The phase transition temperatures of some alkoxy substituted achiral calamitic liquid crystals and the corresponding alkyl substituted and other reference derivatives are presented in tables 1–18 where Cr, SmG, SmF, SmE, SmC, SmC₂, SmC_d, SmC_{mod}, SmB, SmA, SmA_{re}, SmA_{mod}, SmA_d, SmA₁, SmA₂, N_{re}, N, and I denote the crystalline, smectic G, F, E, C, C₂, C_d, modulated C_{mod},

Table 1. Physico-chemical properties of liquid crystals: $Y C_n H_{2n+1} O - \text{C}_6\text{H}_4(K) - \text{COO} - \text{C}_6\text{H}_4(Y) - \text{COO} - \text{C}_6\text{H}_4(Z) - \text{CN})_k - \text{CN}$



Compound	Y	k	Phase transitions/°C	$d_1/\text{Å}$	$d_2/\text{Å}$	d_2/L	Ref.
1-1	C ₄ H ₉ O	1	Cr 78 N (75.5) I				[3]
1-2	C ₅ H ₁₁ O	1	Cr 53 N 67.5 I		24.0–25.0	1.371–1.429	[3, 33]
1-3	C ₆ H ₁₃ O	1	Cr 58 N 76.5 I		27.7	1.351	[3, 34]
1-4	C ₇ H ₁₅ O	1	Cr 53.5 N 75 I				[3]
1-5	C ₈ H ₁₇ O	1	Cr 54.5 Sm 67 N 80 I		32.0 ^b	1.368 ^b	[3, 35]
1-6	C ₄ H ₉	1	Cr 46.5 N (16.5) I				[3]
1-7	C ₅ H ₁₁	1	Cr 22.5 N 35 I	14.3 ^a	24.8 ^a	1.378 ^a	[3, 36]
1-8	C ₆ H ₁₃	1	Cr 13.5 N 27 I		28.0	1.400	[3, 37]
1-9	C ₇ H ₁₅	1	Cr 28.5 N 42 I		29.0	1.381	[3, 38]
1-10	C ₈ H ₁₇	1	Cr 21.5 SmA 33.5 N 40.5 I		31.6 ^b	1.430 ^b	[35, 39]
1-11	C ₂ H ₅ OC ₂ H ₄	1	Cr 50.6 I				[40]
1-12	C ₂ H ₅ OC ₂ H ₄ O	1	Cr 75.5 I				[41]
1-13	C ₅ H ₁₁ O	2	Cr 104 SmF 130 SmB 172 N 253 I		25.5 ^c	1.130 ^c	[42]
1-14	C ₅ H ₁₁	2	Cr 130 N 239 I	20.4	30.9	1.404	[3, 34]
1-15	C ₃ H ₇ OC ₂ H ₄	2	Cr 99.5 N 193.5 I				[40]

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

^b SmA phase.

^c $T_{\text{meas}} = 150^\circ\text{C}$.

 Table 2. Mesomorphic properties of liquid crystals: $Y - \text{C}_6\text{H}_4 - \text{N} - \text{C}_6\text{H}_4 - Z$

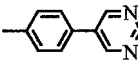
Compound	Y	Z	Phase transitions/°C	Ref.
2-1	C ₅ H ₁₁ O	CN	Cr 59.3 N 94.6 I	[11]
2-2	C ₆ H ₁₃ O	CN	Cr 62.8 N 98.7 I	[11]
2-3	C ₇ H ₁₅ O	CN	Cr 60.2 Sm 89.2 N 99 I	[11]
2-4	C ₈ H ₁₇ O	CN	Cr 66.8 Sm 100.4 N 101.5 I	[11]
2-5	C ₅ H ₁₁	CN	Cr 47.4 N 68 I	[11]
2-6	C ₆ H ₁₃	CN	Cr 42.2 Sm 51.7 N 62.3 I	[11]
2-7	C ₇ H ₁₅	CN	Cr 47.2 Sm 66.8 N 70.3 I	[11]
2-8	C ₈ H ₁₇	CN	Cr 51.1 Sm 72 I	[11]
2-9	C ₅ H ₁₁ O	C ₅ H ₁₁	Cr 55 N 62 I	[43]
2-10	C ₅ H ₁₁	C ₅ H ₁₁	Cr 33 Sm (30.7) I	[43]
2-11	C ₅ H ₁₁	OC ₃ H ₇	Cr 42 I	[44]
2-12	C ₅ H ₁₁	C ₃ H ₇	Cr 20 Sm (5) I	[43]
2-13	C ₅ H ₁₁	OC ₄ H ₉	Cr 38 Sm (34) I	[44]
2-14	C ₅ H ₁₁	C ₄ H ₉	Cr 17.4 N 21.8 I	[45]
2-15	NC	 OC ₄ H ₉	Cr 117 N 265 I	[45]
2-16	NC	 C ₄ H ₉	Cr 95 N 233 I	[45, 46]

smectic B, A, reentrant smectic A, modulated smectic A_{mod}, smectic A_d, A₁, A₂, reentrant nematic, nematic, and isotropic phases, respectively.

2.1. Terminal alkoxy substitution

It is evident from tables 1–4, 6, 7 and 11 that the terminal alkoxylation of achiral calamitic liquid crystals can increase (compounds 1-1 and 1-6; 1-2 and 1-7; 1-3 and 1-8; 1-4 and 1-9; 1-5 and 1-10; 1-13 and 1-14; 2-1–2-4 and 2-5–2-8; 2-9 and 2-10; 2-13 and 2-14; 2-15 and 2-16; 3-2 and 3-5; 3-3 and 3-6; 3-7, 3-8 and

3-10; 3-11 and 3-12; 3-13, 3-14 and 3-16; 4-6 and 4-7; 4-15 and 4-16; 6-1–6-12; 6-13, 6-14 and 6-16; 7-2–7-16; 11-1–11-4) or decrease (compounds 4-13 and 4-14) the clearing points (nematic– or smectic–isotropic phase transition temperatures), or results in the disappearance of the mesophases (compounds 2-11 and 2-12, 4-1 and 4-2), or does not change their isotropic character (compounds 3-1 and 3-4) in comparison with those of the corresponding alkyl derivatives, comparing compounds with the same number of carbon atoms in their alkoxy and alkyl chains. Some of these results do not

Table 3. Mesomorphic properties of liquid crystals: Y  Z







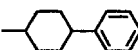




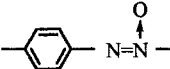
Compound	Y	Z	Phase transitions/°C	Ref.
3-1	C ₅ H ₁₁ O	CN	Cr 100 I	[12]
3-2	C ₆ H ₁₃ O	CN	Cr 88 SmA (83) N 89 I	[12]
3-3	C ₇ H ₁₅ O	CN	Cr 93 SmA 94 I	[12]
3-4	C ₅ H ₁₁	CN	Cr 108.5 I	[47]
3-5	C ₆ H ₁₃	CN	Cr 104 I	[47]
3-6	C ₇ H ₁₅	CN	Cr 107 I	[47]
3-7	C ₆ H ₁₃ O	C ₆ H ₁₃	Cr 44 SmB 59 SmA 89 I	[48]
3-8	C ₆ H ₁₃	OC ₆ H ₁₃	Cr 45 SmA 71 I	[48]
3-9	C ₆ H ₁₃ O	OC ₆ H ₁₃	Cr 71 SmA 104.5 I	[49]
3-10	C ₆ H ₁₃	C ₆ H ₁₃	Cr 30 SmB 42.5 SmA 53 I	[49]
3-11	C ₅ H ₁₁ O	 CN	Cr ₂ 82 Cr ₁ 91.5 Sm 199 N 261 I	[50]
3-12	C ₅ H ₁₁	 CN	Cr 125 N 241 I	[50]
3-13	C ₆ H ₁₃ O	 C ₆ H ₁₃	Cr 76.5 SmG 80 SmF 116.5 SmC 153.2 SmA 206 I	[51]
3-14	C ₆ H ₁₃	 OC ₆ H ₁₃	Cr 75 SmC 151.5 SmA 193 I	[52]
3-15	C ₆ H ₁₃ O	 OC ₆ H ₁₃	Cr 120 SmC 189 SmA 215.5 I	[13]
3-16	C ₆ H ₁₃	 C ₆ H ₁₃	Cr 104 SmA 185 I	[13]

Table 4. Mesomorphic properties of liquid crystals: Y  Z

Compound	Y	Z	Phase transitions/°C	Ref.
4-1	C ₄ H ₉ O	CN	Cr 60 I	[53]
4-2	C ₄ H ₉	CN	Cr 41 N (40.5) I	[54]
4-3	C ₃ H ₇ OCH ₂	CN	Cr 23 I	[53]
4-4	C ₂ H ₅ OC ₂ H ₄	CN	Cr 42 I	[53]
4-5	CH ₃ OC ₃ H ₆	CN	Cr 52 N 55 I	[53]
4-6	C ₅ H ₁₁	OC ₂ H ₅	Cr 51 N (49) I	[10]
4-7	C ₅ H ₁₁	C ₂ H ₅	Cr 5.5 I	[55]
4-8	C ₅ H ₁₁	CH ₂ OCH ₃	Cr 9.5 N (-9) I	[56]
4-9	C ₅ H ₁₁	OC ₄ H ₉	Cr 34 X 46 I ^a	[57]
4-10	C ₅ H ₁₁	CH ₂ OC ₃ H ₇	Cr 25 N (-28) I	[56]
4-11	C ₅ H ₁₁	C ₂ H ₄ OC ₂ H ₅	Cr 4 N (-28) I	[56]
4-12	C ₅ H ₁₁	C ₃ H ₆ OCH ₃	Cr 0 N (-17) I	[56]
4-13	C ₅ H ₁₁	 OCH ₃	Cr 80 N 165 I	[58]
4-14	C ₅ H ₁₁	 CH ₃	Cr 98 Sm 123 N 178 I	[58]
4-15	C ₅ H ₁₁	 OC ₅ H ₁₁	Cr 42 X 183 I ^a	[59]
4-16	C ₅ H ₁₁	 C ₅ H ₁₁	Cr 13 X 166 I ^a	[59]

^a X is an unknown mesophase.

Table 5. Physico-chemical properties of liquid crystals: $C_nH_{2n+1}(O)_k$ -- $(O)_kC_nH_{2n+1}$ [60–75]

Compound	<i>n</i>	<i>k</i>	Phase transitions/°C	$d^a/\text{Å}$	d^a/L	μ/D	ϵ_{\perp}^b	$\Delta\epsilon^b$	g, T_{N-1}	$n_{\perp}^{b,c}$	$\Delta n^{b,c}$	γ_1^f/cP	K_{33}/K_{11}^b	$\rho/g\text{ cm}^{-3}$
5-1	4	1	Cr 102 N 136.7 I	22.78	0.897	2.38	4.550	-0.290	0.87	1.516	0.223	18.0	1.17	1.0269 ^k
5-2	5	1	Cr 75.5 N 123.2 I	22.55	0.805	2.35	4.370	-0.240	0.89	1.515	0.212	20.0	0.91	1.0048 ^l
5-3	6	1	Cr 81 Sm (74) N 129 I	27.00	0.888	2.35	4.140	-0.260	0.89	1.500	0.210	27.0	0.95	0.9884 ^m
5-4	7	1	Cr 74.4 SmC 95.4 N 124.2 I	28.80	0.873	2.36	3.990	-0.280	0.88	1.499	0.193	35.5	0.70	0.9750 ⁿ
5-5	8	1	Cr 79.5 SmC 107.7 N 126.1 I	31.45	0.939					1.489	0.189		0.55	0.9710 ^p
5-6	4	0	Cr 22 N 32 I			1.70	3.913	0.197	0.80	1.545	0.171	29.5 ^e	0.98	1.0277 ^q
5-7	5	0	Cr 24 N 67.5 I			1.70	3.511	0.249	0.81	1.518	0.192	21.7 ^h	0.87	1.0048 ^r
5-8	6	0	Cr 24 Sm (17) N 54.5 I	26.7 ^d	0.960 ^d	1.70	3.470	0.160	0.80	1.518	0.161	25.6 ⁱ	0.75	0.9884 ^s
5-9	7	0	Cr 34 Sm 54.5) N 71 I	28.9 ^d	0.957 ^d	1.70	3.280	0.220	0.82	1.502	0.184	32.0 ^j	0.71	0.9749 ^t
5-10	8	0	Cr 39 Sm 64.5 N 67 I	30.9 ^d	0.945 ^d					1.502	0.148 ^c		0.56 ^c	0.9704 ^u

^a $T_{\text{meas}} = T_{\text{Cr-N}}$ or $T_{\text{Sm-N}} + 5^\circ\text{C}$.




^b $T_{\text{meas}} = T_{\text{N-I}} - 10^\circ\text{C}$.

^c $\lambda = 546\text{ nm}$.

^d Smectic phase.

^e $T_{\text{meas}} = T_{\text{N-I}} - 2^\circ\text{C}$.

^{f,g,h,i,j,k,l,m,n,p,q,r,s,t,u} $T_{\text{meas}} = 110, 28.8, 61.8, 48.7, 62.9, 121.8, 121.2, 120.2, 120.5, 120.3, 27.2, 44.9, 44.5, 56.3, 50.1^\circ\text{C}$, respectively.




 Table 6. Mesomorphic properties of liquid crystals: Y--A--B--Z

Compound	Y	A	B	Z	Phase transitions/°C	$\Delta T/^\circ\text{C}$	Ref.
6-1	$C_8H_{17}O$	COO	—	CN	Cr 97 N _{re} 120 SmA 201 N 240 I	39.0	[76]
6-2	C_8H_{17}	COO	—	CN	Cr 70 SmA 184 N 217 I	33.0	[77]
6-3	$C_8H_{17}O$	COO	CH_2CH_2	CN	Cr 85 N 166 I	81.0	[77]
6-4	C_8H_{17}	COO	CH_2CH_2	CN	Cr 92 N _{re} (72) SmA 96 N 144 I	48.0	[78]
6-5	$C_8H_{17}O$	COO	CH=CH	CN	Cr 95.5 SmA (94.1) N _{re} 137.8 SmA 248.5 N 282.8 I	34.3	[77]
6-6	C_8H_{17}	COO	CH=CH	CN	Cr 105 N 265 I	160.0	[79]
6-7	$C_8H_{17}O$	COO	C≡C	CN	Cr 86 SmA 96 N 248 I	152.0	[77]
6-8	C_8H_{17}	COO	C≡C	CN	Cr 78 SmA (53) N 228 I	150.0	[77]
6-9	$C_8H_{17}O$	COO	COO	CN	Cr 116 N 229 I	113.0	[77]
6-10	C_8H_{17}	COO	COO	CN	Cr 98 N 221 I	123.0	[80]
6-11	$C_8H_{17}O$	COO	N=CH	CN	Cr 98 SmA 119 N _{re} 166 SmA 204 N 264 I	60.0	[81]
6-12	C_8H_{17}	COO	N=CH	CN	Cr 104 SmA (77.6) N _{re} (84) SmA 196 N 246 I	50.0	[81]
6-13	CH_3O	COO	CH=N	CH_3	Cr 129 N 274.5 I	145.5	[82]
6-14	CH_3	COO	CH=N	OCH_3	Cr 135 N 280 I	145.0	[82]
6-15	CH_3O	COO	CH=N	OCH_3	Cr 153.5 N 305 I	151.5	[82]
6-16	CH_3	COO	CH=N	CH_3	Cr 170 N 240 I	70.0	[82]
6-17	C_4H_9O	COO	COO	C_4H_9	Cr 113 N 212 I	99.0	[83]
6-18	C_4H_9	COO	COO	OC_4H_9	Cr 112 N 216 I	104.0	[84]




support the suggestion of Maier and Saupe that increasing the anisotropy of polarizability should enhance the nematic thermostability [105]. In this case, the alkoxy derivatives, which have higher values of polarizability than those of the corresponding alkyl compounds [42, 106], should always exhibit higher clearing temperatures.

It has been proposed that the non-mesomorphic behaviour of compound 4-1 can be caused by the absence of conjugation between the electrons of the oxygen and

cyclohexane fragment, leading to repulsion between the neighbouring molecules, thus increasing the intermolecular separation [1]. The melting temperatures (crystal–smectic or –nematic phase transition temperatures) can be increased (compounds 1-1–1-10; 2-1–2-16; 3-7, 3-8 and 3-10; 4-1 and 4-2; 4-6 and 4-7; 4-15 and 4-16; 6-1 and 6-2; 6-7–6-10; 7-2–7-8 and 7-10–7-16) or decreased (compounds 3-11 and 3-12; 3-13, 3-14 and 3-16; 4-13 and 4-14; 6-3–6-6; 6-11 and 6-12; 6-13, 6-14 and 6-16; 7-1

Table 7. Mesomorphic properties of liquid crystals: Y  COO  OOC  CN

Compound	Y	Phase transitions/°C	ΔT /°C	Ref.
7-1	C ₃ H ₇ O	Cr 186 N > 280 I		[85]
7-2	C ₄ H ₉ O	Cr 176 N > 280 I		[85]
7-3	C ₅ H ₁₁ O	Cr 141.5 SmA 147 N 281 I	134.0	[85]
7-4	C ₆ H ₁₃ O	Cr 141 SmA 159 N 270 I	111.0	[85]
7-5	C ₇ H ₁₅ O	Cr 140 SmA 168 N 262 I	94.0	[85]
7-6	C ₈ H ₁₇ O	Cr 140 SmA 193 N 255 I	62.0	[85]
7-7	C ₉ H ₁₉ O	Cr 140.5 SmA 227 N 249 I	22.0	[85]
7-8	C ₁₀ H ₂₁ O	Cr 139 SmA 232 N 243 I	11.0	[85]
7-9	C ₃ H ₇	Cr 192 N 282 I	90.0	[85]
7-10	C ₄ H ₉	Cr 161 SmA (144) N 268 I	107.0	[85]
7-11	C ₅ H ₁₁	Cr 130 SmA 148.6 N 263 I	114.4	[85]
7-12	C ₆ H ₁₃	Cr 123 SmA 155 N 251 I	96.0	[85]
7-13	C ₇ H ₁₅	Cr 121 SmA 153 N 245 I	92.0	[85]
7-14	C ₈ H ₁₇	Cr 125 SmA 142 N _{re} 157 SmA 186 N 238 I	52.0	[85]
7-15	C ₉ H ₁₉	Cr 126 SmA 213 N 233 I	20.0	[85]
7-16	C ₁₀ H ₂₁	Cr 125.5 SmA 218 N 227 I	9.0	[85]

Table 8. Physico-chemical properties of liquid crystals: C₈H₁₇O  OOC  COO  Z




Compound	Z	Phase transitions/°C	ΔT /°C	$d^a/\text{Å}$	d^a/L	$\Delta\epsilon^b$	Ref.
8-1	OCH ₃	Cr 167 N 218 I	51				[86]
8-2	OC ₂ H ₅	Cr 175 N 222 I	47				[87]
8-3	OC ₃ H ₇	Cr 165 SmA 175 N 208 I	33	32.8	0.997		[87]
8-4	OC ₄ H ₉	Cr 155 SmC 172 SmA 182 N 208 I	26	33.9	0.994		[87]
8-5	OC ₅ H ₁₁	Cr 142 SmC 176 SmA 183 N 200 I	17	34.1	0.963		[87]
8-6	OC ₆ H ₁₃	Cr 145 SmC 177 SmA 183 N 200 I	17	35.2	0.962		[87]
8-7	OC ₇ H ₁₅	Cr 142 SmC 178 SmA 183 N 194 I	11	35.4	0.937		[87]
8-8	OC ₈ H ₁₇	Cr 144 SmC 180 SmA 183 N 191 I	8	36.8	0.944	-0.63	[86, 88]
8-9	CH ₃	Cr 140 N 187 I	47				[86]
8-10	C ₂ H ₅	Cr 154 N 195 I	41				[87]
8-11	C ₃ H ₇	Cr 148 SmA 152 N 193 I	41	31.4	0.991		[87]
8-12	C ₄ H ₉	Cr 133 SmC 142 SmA 157 N 184 I	37	32.9	0.994		[87]
8-13	C ₅ H ₁₁	Cr 133 SmC 150 SmA 160 N 182 I	22	33.9	0.991		[87]
8-14	C ₆ H ₁₃	Cr 129 SmC 152 SmA 163 N 179 I	16	34.4	0.069		[87]
8-15	C ₇ H ₁₅	Cr 134 SmC 154 SmA 164 N 177 I	13	35.8	0.978		[87]
8-16	C ₈ H ₁₇	Cr 138 SmC 158 SmA 167 N 175 I	8	36.2	0.955		[86]

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



$$^b \tau = T_{\text{meas}}/T_{\text{meas}}/T_{\text{N-I}}, K = 0.98.$$

and 7-9; 11-1–11-4) in the alkoxy substituted derivatives compared with those of the corresponding alkyl derivatives. And the nematic ranges (ΔT) can be broader (compounds 1-2 and 1-7; 1-4 and 1-9; 1-5 and 1-10; 2-1 and 2-5; 2-2 and 2-6; 2-3 and 2-7; 2-15 and 2-16; 4-13 and 4-14; 6-1–6-4; 6-7 and 6-8; 6-11 and 6-12; 6-13, 6-14 and 6-16; 7-3–7-8 and 7-11–7-16; 11-3 and 11-4) or narrower (compounds 1-3 and 1-8; 1-13 and 1-14; 3-11 and 3-12; 6-5 and 6-6; 6-9 and 6-10). Terminal alkoxy substitution can increase (compounds 1-13 and 1-14; 2-4 and 2-8; 3-2 and 3-5; 3-3 and 3-6; 3-11 and 3-12; 3-13, 3-14 and 3-16; 4-6 and 4-7; 6-1 and 6-2; 6-5 and 6-6) or decrease (compounds 2-2 and 2-6; 2-11 and 2-12; 3-8 and 3-10;

4-1 and 4-2; 4-13 and 4-14; 6-3 and 6-4; 7-2 and 7-10; 7-6 and 7-14) or keep the same (compounds 1-1–1-10; 2-1 and 2-5; 2-3 and 2-7; 2-15 and 2-16; 3-7 and 3-10; 6-7–6-12; 6-13, 6-14 and 6-16; 7-1 and 7-9; 7-3–7-5 and 7-11–7-13; 7-7 and 7-15; 7-8 and 7-16; 11-1–11-4) number of mesophases in the alkoxy derivatives as those of the corresponding alkyl derivatives. Terminal alkoxylation may give more pronounced nematic (compounds 2-4 and 2-8; 2-9 and 2-10; 4-13 and 4-14; 6-3 and 6-4; 7-2 and 7-10) or smectic (compounds 2-13 and 2-14; 3-2 and 3-5; 3-3 and 3-6; 3-11 and 3-12) character of the mesophases, or change the character of the mesophase from nematic to smectic (compounds 2-13 and 2-14) or

Table 9. Mesomorphic properties of liquid crystals: Y  OOC  COO  Y

Compound	Y	Phase transitions/ $^{\circ}\text{C}$	$\Delta T/^{\circ}\text{C}$	Ref.
9-1	CH_3O	Cr 143 N 243 I	100.0	[89]
9-2	$\text{C}_2\text{H}_5\text{O}$	Cr 141 N 244 I	103.0	[89]
9-3	$\text{C}_3\text{H}_7\text{O}$	Cr 137 N 214 I	77.0	[89]
9-4	$\text{C}_4\text{H}_9\text{O}$	Cr 107 SmA 156 N 209 I	53.0	[89]
9-5	$\text{C}_5\text{H}_{11}\text{O}$	Cr ₂ 85 Cr ₁ 101 SmB 105 SmA 173 N 193 I	20.0	[89]
9-6	$\text{C}_6\text{H}_{13}\text{O}$	Cr ₂ 86 Cr ₁ 97 Sm 98 SmB 108 SmA 181 N 188 I	7.0	[89]
9-7	$\text{C}_7\text{H}_{15}\text{O}$	Cr ₂ 77 Cr ₁ 95 Sm 96 SmB 107 SmC 111 SmA 180 I		[89]
9-8	$\text{C}_8\text{H}_{17}\text{O}$	Cr ₂ 73 Cr ₁ 91 Sm 93 SmB 111 SmC 119 SmA 179 I		[89]
9-9	CH_3	Cr 177.7 N 193.5 I	15.8	[90]
9-10	C_2H_5	Cr 111.8 N 161.1 I	49.3	[90]
9-11	C_3H_7	Cr 116 N 173.5 I	57.5	[90]
9-12	C_4H_9	Cr 92.6 SmB (82) SmA 108.2 N 151 I	42.8	[90]
9-13	C_5H_{11}	Cr 95.3 SmB (92.1) SmA 128.8 N 153.6 I	24.8	[90]
9-14	C_6H_{13}	Cr 74.3 SmB 106.7 SmA 138.5 N 142.4 I	3.9	[90]
9-15	C_7H_{15}	Cr 69.6 SmB 111.1 SmA 142.3 I		[90]
9-16	C_8H_{17}	Cr 70.8 SmB 114.8 SmA 139.6 I		[90]

Table 10. Physico-chemical properties of liquid crystals: Y  A  CN

Compound	Y	A	Phase transitions/ $^{\circ}\text{C}$	$d_2/\text{\AA}$	d_2/L	Ref.
10-1	C_5H_{11}	CH_2O	Cr 74.3 N (48.6) I			[4]
10-2	C_5H_{11}	$\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$	Cr 62 N (54) I			[91]
10-3	C_5H_{11}	CH_2CH_2	Cr 30 N 51 I			[92]
10-4	C_5H_{11}	$\text{CH}=\text{CH}$	Cr 53.5 N 107.2 I			[93]
10-5	C_5H_{11}	$\text{CH}=\text{CHCH}_2\text{CH}_2$	Cr 40 N (39) I			[94]
10-6	C_5H_{11}	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$	Cr 51 N (39) I			[94]
10-7	C_5H_{11}	$\text{CH}=\text{CHCH}_2\text{O}$	Cr 64 N (43) I			[94]
10-8	C_5H_{11}	$\text{C}\equiv\text{C}$	Cr 41.4 N 72.5 I			[93]
10-9	C_5H_{11}	COO	Cr 47.2 N 79.2 I	26.8 ^a	1.521 ^a	[95, 96]
10-10	C_5H_{11}	OOC	Cr 74.4 N (67.4) I			[97]
10-11	C_5H_{11}	COS	Cr 88 N 99 I			[98]
10-12	C_5H_{11}	OOCCH=CH	Cr 122 N (109) I			[99]
10-13	C_5H_{11}	—	Cr 30 N 55 I			[54]
10-14	C_7H_{15}	CH_2O	Cr 46 N 53 I	32.2	1.451	[34]
10-15	C_7H_{15}	—	Cr 30 N 59 I	25.9 ^a	1.438 ^a	[36, 54]

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

from smectic to nematic (compounds **2-9** and **2-10**) in comparison with those of the corresponding alkyl derivatives.



In particular, the reentrant nematic phase can be more favourable for the alkoxy (compounds **6-1** and **6-2**; **6-5** and **6-6**) or alkyl (compounds **6-3** and **6-4**; **7-6** and **7-14**) or both derivatives (compounds **6-11** and **6-12**). In other words, the reentrant nematic phase can be formed in three-ring octyloxy and the corresponding octyl substituted cyano derivatives which have the following combinations A, B of the linkages: COO, SG; COO, CH=CH; COO, N=CH and COO, CH₂CH₂; COO, N=CH; COO, OOC, respectively, where SG is the single carbon-carbon bond.

For the octyloxy derivatives the thermal efficiency of the reentrant nematic phase (T_{Nre}) is consistent with the following order (compounds **6-1**, **6-5**, **6-11**, table 6 and [81]):

$$T_{\text{Nre}} \rightarrow \text{A, B: COO, SG} < \text{COO, CH=CH} < \text{CH=N,}$$




$$\text{COO} < \text{COO, CH=N} < \text{COO, N=CH}$$

These results reveal that the introduction of the second linking group B (CH=CH, CH=N, N=CH) into the molecular structure of three-ring octyloxy substituted cyano derivatives with one COO linkage A significantly increases the reentrant nematic thermostability.

Table 11. Physico-chemical properties of liquid crystals: C_5H_{11}  A  Z

Compound	A	Z	Phase transitions/ $^{\circ}C$	$d_2/\text{\AA}$	d_2/L	Ref.
11-1	COO	OCH ₃	Cr 40.9 N 71.3 I	29.0 ^a	1.526 ^a	[9, 96]
11-2	COO	CH ₃	Cr 47.5 N (45) I			[100]
11-3	COO	OC ₅ H ₁₁	Cr 34.1 N 75.9 I			[101]
11-4	COO	C ₅ H ₁₁	Cr 37 N 47 I			[102]
11-5	CH ₂ O	OCH ₃	Cr 46 N (38) I			[103]
11-6	CH ₂ CH ₂ CH ₂ O	OCH ₃	Cr 47 N (46) I			[6]
11-7	CH=CHCH ₂ O	OCH ₃	Cr 44 N 46 I			[6]
11-8	C≡C	OCH ₃	Cr 30.9 N 45.7 I			[55]
11-9	CH ₂ CH ₂ CH ₂ CH ₂	OCH ₃	Cr 27 SmB (16) I			[6]
11-10	CH=CHC≡C	OCH ₃	Cr 35.3 N 117.3 I			[104]
11-11	CH ₂ CH ₂	OCH ₃	Cr 30 N 34 I			[103]
11-12	CH=CH	OCH ₃	Cr 49 N 97 I			[98]
11-13	CH=CHCH ₂ CH ₂	OCH ₃	Cr 25 N 34 I			[6]
11-14	—	OCH ₃	Cr 41 N (31) I			[7]

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

Table 12. Mesomorphic properties of liquid crystals: C_5H_{11}  A  B  CN




Compound	A	B	Phase transitions/ $^{\circ}C$	$\Delta T/^{\circ}C$	Ref.
12-1	CH ₂ O	—	Cr 107 SmA 136.3 N 193.2 I	56.9	[4]
12-2	CH ₂ CH ₂ CH ₂ O	—	Cr 83 SmA 149 N 167 I	18.0	[91]
12-3	CH ₂ CH ₂	—	Cr 79 SmA 86 N 184 I	98.0	[131]
12-4	COO	—	Cr 85.2 N 240.8 I	155.6	[4]
12-5	CH ₂ CH ₂ CH ₂ O	COO	Cr 82 SmA 117 N 168 I	51.0	[94]
12-6	CH ₂ CH ₂	COO	Cr 79.2 N 189.4 I	110.2	[132]
12-7	COO	COO	Cr 88 N 252 I	164.0	[80]
12-8	CH ₂ CH ₂ CH ₂ CH ₂	COO	Cr 78 N 151 I	73.0	[94]
12-9	CH=CHCH ₂ O	COO	Cr 79 N 170 I	91.0	[94]
12-10	CH=CHCH ₂ CH ₂	COO	Cr 76 N 171 I	95.0	[94]
12-11	—	COO	Cr ₂ 82 Cr ₁ 111 N 225.5 I	114.5	[133]
12-12	—	—	Cr 96 N 222 I	126.0	[134]

A highly nematic character of the mesophases can be observed in octyloxy and the corresponding octyl-substituted cyano derivatives which have the following combinations of linkages A, B: COO, CH₂CH₂; COO, COO and COO, CH=CH; COO, COO (respectively compounds **6-3**, **6-9** and **6-6**, **6-10**, table 6). This shows that the presence of the COO group as linkage A in the molecular core of the octyloxy and the corresponding octyl-substituted cyano derivatives is essential for the formation of the nematic phase alone.




The importance of the position of the terminal alkoxy group for the mesomorphic properties of LCs is clearly shown in table 3. So far the attachment of the hexyloxy group to the pyrimidine ring of two-ring compound **3-8** increases the clearing and melting points and results in the disappearance of the smectic B phase; while the same attachment of the hexyloxy group to the phenyl fragment of compound **3-7** further increases the clearing temper-

ature, and enhances the smectic B thermostability and the melting point (which is slightly lower than that of compound **3-8**) compared with those of the parent compound **3-10**. Similar conclusions can be derived for three-ring derivatives **3-13**, **3-14**, **3-16** which are presented in table 3. As can be seen from table 6, the attachment of the butyloxy group to the position close to the carbonyl part of the ester linkage of compound **6-18** gives a higher nematic thermostability and a lower crystal–nematic phase transition temperature, in comparison with those of the corresponding derivative **6-17** with the opposite orientations of the ester linkages. These results reveal the importance of the molecular structure of the alkoxy derivatives for their mesomorphic behaviour.

It is evident from tables 4, 10 and 11 that alkoxy derivatives **4-6**, **4-9** and **11-1**, **11-3** exhibit lower clearing temperatures than the corresponding cyano derivatives

Table 13. Mesomorphic properties of liquid crystals: $C_8H_{17}O$  A  B  CN

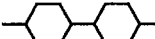

Compound	A	B	Phase transitions/ $^{\circ}C$	$\Delta T/^{\circ}C$	Ref.
13-1	—	OCH ₂	Cr 129 SmG (119) N 171 I	42.0	[122]
13-2	—	COO	Cr 114 N 227.5 I	113.5	[77]
13-3	—	OOC	Cr 128 SmC _{mod} (123) SmA _d 159 N 236 I	77.0	[122]
13-4	—	CH ₂ CH ₂	Cr 91.8 SmA (<80) N 155.9 I	64.1	[130]
13-5	OOC	OCH ₂	Cr 114.5 SmC _{mod} (110.5) SmA ₁ 122 N 167 I	45.0	[122]
13-6	OOC	OOC	Cr 129 SmA _d 199 N 241 I	42.0	[122]
13-7	OOC	COO	Cr 148 SmA 158 N 233 I	75.0	[125]
13-8	OOC	N=CH	Cr 113 SmA _{mod} 132 SmA ₁ 149 N 266 I	117	[81]
13-9	OOC	CH=N	Cr 102 SmC ₂ (99) SmC _{mod} 108 SmC 109 SmA 206 N 258 I	52.0	[81]
13-10	N=CH	OCH ₂	Cr 112 SmB 122 SmB _{hex} 124 SmA 138 N 191 I	53.0	[122]
13-11	N=CH	COO	Cr 133 N 255 I	12.2	[81]
13-12	N=CH	OOC	Cr 122 SmC _{mod} (119) SmA 172 N 262 I	90.0	[81]
13-13	CH=N	—	Cr 68 SmE 100 SmA 243 N 267 I	24.0	[129]
13-14	CH=CHCOO	—	Cr 135 SmB (93) SmA 247 N > 290 I		[128]
13-15	CH ₂ CH ₂	—	Cr 72.5 SmA 144 N 148 I	4.0	[130]
13-16	COO	CH=N	Cr 108 N _{re} 153 SmA 198 N 255 I	57.0	[81]
13-17	CH=N	COO	Cr 113 N _{re} 138 SmA _d 208 N 254 I	46.0	[81]
13-18	CH=N	OOC	Cr 119 SmA ₁ 147 N 266 I	119.0	[81]

Table 14. Mesomorphic properties of liquid crystals: C_5H_{11}  A  B  C_5H_{11}

Compound	A	B	Phase transitions/ $^{\circ}C$	$\Delta T/^{\circ}C$	Ref.
14-1	CH ₂ O	—	Cr 70 SmB 133 N 143 I	10	[6]
14-2	CH ₂ CH ₂ CH ₂ O	—	Cr 67 SmB 113 N 127 I	14	[6]
14-3	CH ₂ CH ₂	—	Cr 23 Sm 135 N 136 I	1	[180]
14-4	CH ₂ CH ₂ CH ₂ CH ₂	—	Cr 50 SmB 111 I		[6]
14-5	COO	—	Cr 112 N 179 I	67	[181]
14-6	OOC	—	Cr 70 Sm 90 N 156 I	66	[182]
14-7	CH=CHCH ₂ O	—	Cr 56 Sm 109 SmB 113 N 136 I	23	[6]
14-8	CH ₂ O	CH ₂ CH ₂ CH ₂ CH ₂	Cr 42 SmB 108 I		[183]
14-9	CH ₂ CH ₂ CH ₂ O	CH ₂ CH ₂ CH ₂ CH ₂	Cr 52 SmB 94 I		[183]
14-10	COO	CH ₂ CH ₂ CH ₂ CH ₂	Cr 59 SmB 135 N 139 I	4	[183]
14-11	CH=CHCH ₂ O	CH ₂ CH ₂ CH ₂ CH ₂	Cr 77 Sm 94 SmB 99 N 107 I	8	[183]
14-12	CH ₂ O	OCH ₂ CH ₂ CH ₂	Cr 104 SmA 116 N 124 I	8	[91]
14-13	CH ₂ CH ₂ CH ₂ O	OCH ₂ CH ₂ CH ₂	Cr 108 SmA 112 N 115 I	3	[91]
14-14	CH ₂ CH ₂	OCH ₂ CH ₂ CH ₂	Cr 86 SmB 109 N 117 I	8	[91]
14-15	COO	OCH ₂ CH ₂ CH ₂	Cr 88 Sm 102 SmB 114 SmA 127 N 150 I	23	[91]
14-16	—	—	Cr 50 Sm 196 I		[184]

10-13 and 10-9, respectively. Melting temperatures of alkoxy derivatives can be higher (compounds 4-6, 4-9 and 10-13) or lower (compounds 11-1, 11-3 and 10-9) than those of the corresponding cyano derivatives. These findings for compounds 4-6, 4-9, 10-13, and the above discussed results on the melting points for other alkoxy derivatives, do not support the suggestion that increasing the polarity of the terminal substituents [107] should increase the melting temperatures of liquid crystals [108]. Similar comparisons of the mesomorphic properties of the alkoxy derivatives and the corresponding cyano, nitro and halogen derivatives have been reported in [19, 86, 109–112].

The odd–even effect in the clearing temperatures has been observed for many homologous series of alkyl-substituted liquid crystalline derivatives [1, 3, 14–16, 46, 113, 114]. The odd carbon atom alkyl chain has a terminal CH₃ group which extends the long molecular axis, whereas in an even number carbon chain the terminal CH₃ group tends to lie off axis [16]. In homologous series of alkyl-substituted LCs with alkyl groups longer than propyl, a regular alternation of the nematic–isotropic phase transition temperature can be observed with higher values for the odd homologues (compounds 1-6–1-10, 2-5–2-8, 7-9–7-16, 8-11–8-16, tables 1, 2, 5, 7, 8 and [1, 3, 14–16, 46, 113, 114]). In

Table 15. Physico-chemical properties of liquid crystals: R  B  Z, R = C₅H₁₁




Compound	B	Z	Phase transitions/°C	$\Delta T/^\circ\text{C}$	$\Delta\epsilon^a$	Δn^b	Ref.
15-1	CH ₂ O	OCHF ₂	Cr 52 Sm 76.7 N 142.5 I	65.8	2.4	0.094	[5]
15-2	COO	OCHF ₂	Cr 61 SmB 93 N 196.9 I	103.9	2.5		[5, 185]
15-3	CH ₂ CH ₂	OCHF ₂	Cr 24 SmB 129 N 149.9 I	20.9	7.6 ^b	0.097	[185]
15-4	—	OCHF ₂	Cr 37 SmB 102 N 170 I	68.0	8.9 ^b	0.107	[185]
15-5	CH ₂ O	CF ₃	X 89 N 115 I ^d	26.0			[186]
15-6	COO	CF ₃	X 72 SmB 108 N 160 I ^d	52.0			[186]
15-7	CH ₂ CH ₂	CF ₃	Cr 55 Sm 100 N 123 I	23.0			[187]
15-8	—	CF ₃	X 43 SmB 109 N 123 I ^d	14.0			[186]
15-9	CH ₂ CH ₂ CH ₂ O	F	Cr 69 SmB 95 N 127 I	32.0			[91]
15-10	CH ₂ CH ₂	F	Cr 39 SmB 107 N 140 I	33.0			[7]
15-11	CH=CHCH ₂ O	F	Cr 68 SmB (60) N 131 I	63.0			[188]
15-12	—	F	Cr 69.4 Sm 74.5 N 157.5 I	83.0			[189]
15-13 ^c	CH ₂ O	F	Cr 82.2 N 131.7 I	49.5			[8]
15-14 ^c	OCH ₂	F	Cr 37.7 N 92.8 I	55.1			[8]

^a $\tau = T_{\text{meas}}/T_{N-1}$, $K = 0.85$.

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

^c R is CH₂=CH-C₂H₄.

^d X is an unknown phase.




Table 16. Mesomorphic properties of liquid crystals: Y  COO  B 

Compound	Y	Z	K	M	B	Phase transitions/°C	Ref.
16-1	CH ₃ O	OCH ₃	H	H	OOC	Cr 217.5 SmA (175) N 299 I	[225]
16-2	CH ₃ O	OCH ₃	H	OCH ₃	OOC	Cr 169 N 207.4 I	[226]
16-3	CH ₃ O	OCH ₃	H	CH ₃	OOC	Cr 169 SmA (123) N 252 I	[225]
16-4	CH ₃ O	OCH ₃	H	C ₃ H ₇	OOC	Cr 127 N 135.5 I	[227]
16-5	CH ₃ O	OCH ₃	H	F	OOC	Cr 173.8 Sm (140) N 278.5 I	[228]
16-6	CH ₃ O	OCH ₃	H	Cl	OOC	Cr 173.5 SmA (124.5) N 253 I	[225]
16-7	CH ₃ O	OCH ₃	H	Br	OOC	Cr 170 Sm (130) N 249.5 I	[225]
16-8	CH ₃ O	OCH ₃	H	I	OOC	Cr 173.4 N 222.9 I	[228]
16-9	CH ₃ O	OCH ₃	H	CN	OOC	Cr 202 N 247 I	[80]
16-10	C ₆ H ₁₃ O	CN	OCH ₃	H	COO	Cr 111 N 173 I	[229]
16-11	C ₇ H ₁₅ O	CN	OCH ₃	H	COO	Cr 117 N 165 I	[229]
16-12	C ₈ H ₁₇ O	CN	OCH ₃	H	COO	Cr 112 N _{re} (49) SmA _d 139 N 163 I	[229]
16-13	C ₉ H ₁₉ O	CN	OCH ₃	H	COO	Cr 117 SmA _d 151 N 159 I	[229]
16-14	C ₁₀ H ₂₁ O	CN	OCH ₃	H	COO	Cr 115 SmA _d 157 I	[229]
16-15	C ₆ H ₁₃ O	CN	H	H	COO	Cr 133 SmB (100) N 248 I	[230]
16-16	C ₉ H ₁₉ O	CN	H	H	COO	Cr 121 N _{re} (116) SmA 198 N 229 I	[231]
16-17	C ₁₀ H ₂₁ O	CN	H	H	COO	Cr 108 N _{re} (94.5) SmA 208 N 222 I	[77]




the corresponding alkoxy-substituted series, the oxygen is equivalent to a CH₂ group (from the geometrical point of view, see §1) and the reverse situation has been found with higher clearing points observed for even homologues (compounds 1-1–1-5 and 1-6–1-10, 2-1–2-4, 7-1–7-8, 8-3–8-8, tables 1, 2, 5, 7, 8 and [1, 3, 14–16]). In other words, in most cases the introduction of a CH₂ unit or oxygen atom into the alkyl chain leads to opposite effects on the clearing temperatures of LCs. Increasing the length of alkoxy(alkyl) chains usually lowers the amplitude of alternation of the T_{N-1} , and it

can increase (compounds 1-1–1-10, 2-1–2-8, 3-1–3-3) or lower (compounds 7-1–7-16, table 7) the clearing points, see also [1, 3, 14–16, 46, 113, 114]. These phenomena have attracted much interest [1, 115–118] and been explained in terms of changes in the anisotropy of polarizability [115, 118], and packing efficiency [1]. The influence of intrachain flexibility constraints on the odd–even effects has been discussed in [28, 32].

The effect of terminal alkoxylation and the corresponding alkylation on the phase appearance between the crystalline and isotropic states in some homologous

Table 17. Physico-chemical properties of liquid crystals: Y —— OOC —— OOC —— Z

Compound	Y	Z	K	L	Phase transitions/°C	$d_{smc}/\text{Å}$	d_{smc}/L	Ref.
17-1	C ₈ H ₁₇ O	CN	H	H	Cr 129 SmA _d 199 N 241 I			[123]
17-2	C ₈ H ₁₇ O	CN	H	OC ₂ H ₅	Cr 138 N 143 I			[232]
17-3	C ₈ H ₁₇ O	CN	H	OC ₃ H ₇	Cr 125 N (123) I			[232]
17-4	C ₈ H ₁₇ O	CN	H	OC ₄ H ₉	Cr 105 SmC 110 N 122 I			[233]
17-5	C ₈ H ₁₇ O	CN	H	OC ₅ H ₁₁	Cr 92 SmC 116 N 120 I	28.5	0.990	[232]
17-6	C ₈ H ₁₇ O	CN	H	OC ₆ H ₁₃	Cr 100 SmC 119 N 120 I	20.2	0.980	[232, 223]
17-7	C ₈ H ₁₇ O	CN	H	OC ₈ H ₁₇	Cr 103 SmC 127 I	30.7	0.994	[232]
17-8	C ₈ H ₁₇ O	CN	H	OC ₁₄ H ₂₉	Cr 98 SmC 129 I	35.7	1.008	[232]
17-9	NC	OC ₃ H ₇	H	OC ₃ H ₇	Cr 130 N 132 I			[234]
17-10	NC	OC ₄ H ₉	H	OC ₄ H ₉	Cr 129 N 131 I			[234]
17-11	NC	OC ₅ H ₁₁	H	OC ₅ H ₁₁	Cr 131 SmA (117) N (123) I			[234]
17-12	NC	OC ₆ H ₁₃	H	OC ₆ H ₁₃	Cr 127 SmA 128 N 128 I			[234]
17-13	NC	OC ₇ H ₁₅	H	OC ₇ H ₁₅	Cr 124 SmA 137 I			[234]
17-14	NC	OC ₈ H ₁₇	H	OC ₈ H ₁₇	Cr 121 SmA 134 I			[234]
17-15	NC	OC ₉ H ₁₉	H	OC ₉ H ₁₉	Cr 120 SmA 132 I			[234]
17-16	NC	OC ₁₀ H ₂₁	H	OC ₁₀ H ₂₁	Cr 120 SmA 131 I			[234]
17-17	C ₈ H ₁₇ O	CH ₃	H	OC ₂ H ₅	Cr 97 N (94) I			[235]
17-18	C ₈ H ₁₇ O	H	CH ₃	OC ₂ H ₅	Cr 103 N (100) I			[235]

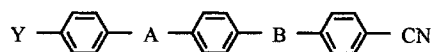
 Table 18. Physico-chemical properties of liquid crystals: C₉H₁₉O——COO——COO——CN

Compound	K	Y	Z	L	Phase transitions/°C	$d^a/\text{Å}$	d^a/L	Ref.
16-13	OCH ₃	H	H	H	Cr 117 SmA _d 151 N 159 I	40.12	1.29	[231]
16-16	H	H	H	H	Cr 121 N _{re} (116) SmA _d 198 N 229 I	40.87	1.31	[231]
18-1	Cl	H	H	H	Cr 115 SmA (85) SmA _d 167 N 186 I	40.49	1.30	[231]
18-2	Br	H	H	H	Cr 96 SmA (83) SmA _d 155 N 181 I	42.04	1.35	[231]
18-3	NO ₂	H	H	H	Cr 111 SmA _d 136 N 157 I	40.12	1.29	[231]
18-4	H	H	OCH ₃	H	Cr 116 N 153 I			[229]
18-5	H	H	Br	H	Cr 95 N 164 I			[229]
18-6	H	H	NO ₂	H	Cr 76 SmC ₂ (56) N 156 I			[229]
18-7	H	H	H	OCH ₃	Cr 70 N 90 I			[229]
18-8	H	H	H	Br	Cr 122 N _{re} (117) SmA _d 199 N 229 I			[229]
18-9	H	OC ₄ H ₉	OCH ₃	H	Cr 69 N (56) I			[234]

^a $T_{meas} = T_{N-1} - 40^\circ\text{C}$.

series of three-ring cyano derivatives can be described by the following system data (as before *SG* in the single carbon-carbon bond).

System (I)



(a) A is *SG*, B is *SG* [3, 42, 119]

Y = C_nH_{2n+1}O n = 3 phases SmB, N
 n = 4 Sm, N
 n = 5–7 SmF, SmB, N
 Y = C_nH_{2n+1} n = 3–6 N
 n = 7 SmA, N

(b) A is COO, B is CH=CH [77, 79]

Y = C_nH_{2n+1}O n = 5–7 phase SmA, N
 n = 8, 9 SmA, N_{re}, SmA, N
 n = 10 N_{re}, SmA, N
 Y = C_nH_{2n+1} n = 5–8 N

(c) A is COO, B is C≡C [77]

Y = C_nH_{2n+1}O n = 5–8 SmA, N
 n = 9 SmA, N_{re}, SmA, N
 n = 10 N_{re}, SmA, N
 Y = C_nH_{2n+1} n = 5 N
 n = 6–9 SmA, N
 n = 10 N_{re}, SmA, N

- (d) A is COO, B is CH=N [81, 120]
 $Y = C_nH_{2n+1}O$ $n = 4-7$ SmA, N
 $n = 8$ N_{re}, SmA, N
 $n = 9$ SmA, N_{re}, SmA, N
 $n = 10$ N_{re}, SmC, SmA, N
 $Y = C_nH_{2n+1}$ $n = 4-6$ N
- (e) A is COO, B is N=CH [81]
 $Y = C_nH_{2n+1}O$ $n = 3$ N
 $n = 4-7$ SmA, N
 $n = 8-10$ SmA, N_{re}, SmA, N
 $n = 11$ SmC, SmA, N
 $Y = C_nH_{2n+1}$ $n = 3$ N
 $n = 4-7$ SmA, N
 $n = 8$ SmA, N_{re}, SmA, N
 $n = 9, 10$ SmA, N
- (f) A is COO, B is COO [77, 80, 121]
 $Y = C_nH_{2n+1}O$ $n = 8$ N
 $n = 9-11$ N_{re}, SmA, N
 $n = 12$ N_{re}, SmA
 $Y = C_nH_{2n+1}$ $n = 8$ N
 $n = 11$ SmA, N
 $n = 12$ SmA
- (g) A is OOC, B is OOC [122, 123]
 $Y = C_nH_{2n+1}O$ $n = 6$ SmA₂, N
 $n = 7$ SmA₂, SmA_d, N
 $n = 8$ SmA_d, N
 $n = 9$ SmC, SmA_d, N
 $Y = C_nH_{2n+1}$ $n = 6$ SmA₂, N
 $n = 7, 8$ SmA₂, SmA_d, N
- (h) A is COO, B is SG [76, 77]
 $Y = C_nH_{2n+1}O$ $n = 7$ N
 $n = 8, 9$ N_{re}, SmA, N
 $n = 10-12$ SmA, N
 $Y = C_nH_{2n+1}$ $n = 7$ N
 $n = 8-10$ SmA, N
- (i) A is OOC, B is OCH₂ [122]
 $n = 6, 7$ SmA₁, N
 $n = 8$ SmC_{mod}, SmA₁, N
 $n = 9$ SmA₂, SmC_{mod}, SmA₁, N
 $n = 10$ SmA₂, SmC_{mod}, SmA_d, N
 $n = 11$ SmA₂, SmA_d, N
- (j) A is N=CH, B is OCH₂ [122]
 $n = 6, 7$ SmB, SmA, N
 $n = 8$ SmB, SmB_{hex}, SmA, N
 $n = 9$ SmB, SmC_{mod}, SmC, SmA, N
 $n = 10, 11$ SmB, SmC_{mod}, SmA, N
 $n = 12$ SmC_{mod}, SmA
- (k) A is SG, B is OCH₂ [122]
 $n = 5, 6$ SmH, SmG, SmA, N
 $n = 7$ SmH, SmG, SmC, N
 $n = 8$ SmG, N
 $n = 9$ SmA, N
 $n = 10-12$ SmA
- (l) A is SG, B is OOC [122, 124]
 $n = 5, 6$ SmB, SmA₁, N
 $n = 7$ SmA, N
 $n = 8$ SmC_{mod}, SmA₁, N
 $n = 9$ SmC_{mod}, SmA_d, N
 $n = 10, 11$ SmC, SmC_{mod}, SmA_d, N
 $n = 12$ SmC, SmA_d
- (m) A is CH=N, B is COO [81]
 $n = 1-7$ N
 $n = 8$ N_{re}, SmA_d, N
 $n = 9$ N_{re}, SmC, SmA_d, N
 $n = 10, 11$ SmA_d, N
- (n) A is CH=N, B is OOC [81]
 $n = 4-8$ SmA₁, N
 $n = 9$ SmA₁, N_{re}, SmA, N
 $n = 10$ SmC₂, SmC, SmA, N
 $n = 11$ SmC₂, SmA, N
- (o) A is OOC, B is N=CH [81]
 $n = 6, 7$ SmA₁, N
 $n = 8$ SmA_{mod}, SmA₁, N
 $n = 9, 10$ SmA₂, SmC_{mod}, SmA, N
- (p) A is N=CH, B is OOC [81]
 $n = 4-7$ SmA, N
 $n = 8, 9$ SmC_{mod}, SmA, N
 $n = 10, 11$ SmC₂, SmC_{mod}, SmA, N
 $n = 12$ SmC₂, SmA, N
- (q) A is OOC, B is CH=N [81]
 $n = 7$ SmC_{mod}, SmA, N
 $n = 8$ SmC₂, SmC_{mod}, SmC, SmA, N
 $n = 9, 10$ SmC₂, SmA, N
 $n = 11, 12$ SmC₂, SmA
- (r) A is N=CH, B is COO [81]
 $n = 7, 8$ N
 $n = 9, 10$ SmA, N
- (s) A is OOC, B is COO [125]
 $n = 7$ N
 $n = 8, 9$ SmA, N
- (t) A is SG, B is COO [77, 126, 127]
 $n = 6-8$ N
 $n = 9$ SmA, N

For the alkoxy derivatives ($Y = C_nH_{2n+1}O$):

- (u) A is CH=CH-COO, B is SG [128]
 $n = 7$ SmA_{re}, N_{re}, SmA, N
 $n = 8, 9$ SmB, SmA, N
 $n = 10$ SmA, N
- (v) A is CH=N, B is SG [129]
 $n = 5$ SmE, N
 $n = 6$ SmB, N
 $n = 7$ SmE, SmB, N_{re}, SmA, N
 $n = 8, 9$ SmE, SmA, N
- (w) A is CH₂CH₂, B is SG [130]
 $n = 2-6$ N
 $n = 7, 8$ SmA, N
- (y) A is SG, B is CH₂CH₂ [130]
 $n = 3-8$ SmA, N

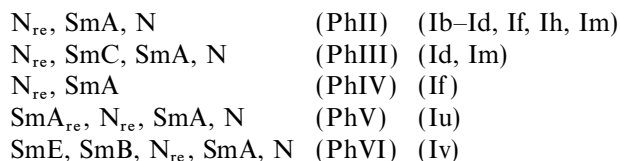
These results and the data presented in tables 6, 7, 13 reveal that the alkoxylation of the system (I) compounds without linking groups or having one linking group A (CH₂CH₂) or B (OCH₂, OOC, COO, CH₂CH₂) does not promote the formation of the reentrant nematic phases (Ia, Ik, Il, It, Iw, Iy). The reentrant nematic phase can be formed in the alkoxy-substituted system (I) having the following combinations of two linking groups A, B: COO, CH=CH; COO, C≡C; COO, CH=N; COO, N=CH; COO, COO; CH=N, COO; CH=N, OOC (Ib–If, Im, In) or having one linkage A: COO, CH=CHCOO, CH=N (Ih, Iu, Iv).

The reentrant nematic phase appears from the heptyloxy homologue (A is CH=CHCOO, CH=N; B is SG; Iu, Iv). Terminal alkoxylation of the system (I) incorporating the following combinations A, B: COO, CH=CH; COO, CH=N; COO, N=CH; COO, SG; CH=N, COO, results in the creation of the reentrant nematic phase in the octyloxy homologue (Ib, Id, Ie, Ih, Im). The formation of the reentrant nematic phase in the nonyloxy homologue and above can be observed in system (I) having COO, C≡C; COO, COO; CH=N, OOC linking groups A, B (Ic, If, In). This phase can be observed in one (A, B are CH=N, OOC; CH=CHCOO, SG; CH=N, SG; In, Iu, Iv), two (A, B are COO, C≡C; COO, SG; CH=N, COO; Ic, Ih, Im), three (A, B are COO, CH=CH; COO, CH=N; COO, N=CH; Ib, Id, Ie), and four (A, B is COO, COO; If) members of the homologous series. It means that COO, COO and CH=N, OOC; CH=CHCOO, SG; CH=N, SG combinations of the linkages are the most and least favourable, respectively for the creation of reentrant nematic phases in the system (I). The introduction of the OCH₂ group as linkage B or in combination with other linking groups in system (I) does not encourage the appearance of the N_{re} phase (Ii–Ik).

Alkoxy-substituted three-ring cyano derivatives of the system (I) which exhibit the reentrant nematic phase can show the following phase sequences between the crystalline and isotropic states:



This phase sequence can appear firstly (Ib, Ic, Ie) or secondly (Id) among the phase sequences containing the N_{re} phase in the homologous series with increasing alkoxy chain length. Some other phase sequences contain the N_{re} phase:



The phase sequence PhII can be observed before (Id) or after PhI (Ib, Ic). While PhIII can be seen after PhI (Id) or after PhII (Im), and PhIV can appear after PhII (If).

It should be mentioned that if the reentrant nematic phases have already disappeared with increasing length of the alkoxy chains, they will not be observed again in higher members of the homologous series. Similar conclusions can be derived for the corresponding alkyl derivatives (see system (I) and tables 6, 7) which show a later and less pronounced appearance of the reentrant nematic phase in comparison with the alkoxy derivatives. One more important thing is: only two combinations COO, C≡C and COO, N=CH of the linkages A, B provide the simultaneous (but different in development) existence of the N_{re} phases in the corresponding alkoxy and alkyl derivatives (Ic, Ie).

The reentrant SmA_{re} phase has been recorded for only the heptyloxy homologue of the system (Iu) which has the CH=CHCOO group as a linkage A. Similar behaviour has been recorded for the modulated smectic C_{mod} and A_{mod} phases in the system (I), with less pronounced appearance in the latter ones (Ii, Ij, Il, Io–Iq). Interestingly, only the combination OOC, N=CH of the A, B linkages provides the modulated phases SmA_{mod} and then –SmC_{mod} with increasing alkoxy chain length within the same homologous series (Io). The results obtained for the system (I) show that the SmC_{mod} phase cannot be observed in homologues lower than heptyloxy. The phase sequences containing the SmC_{mod} phase are more rich and diverse than those which have the N_{re} phase. In some cases we can see the development of the smectic A phase with increasing length of alkoxy chain (from SmA₁ to SmA_d phase), while other phases including the SmC_{mod} remain the same, respectively (Ii, Il).

Let us now consider the effect of alkoxylation of both terminal positions of liquid crystal molecules.

As is evident from tables 3, 5, 6, 8, 9, symmetrical di-alkoxylation increases the clearing points (compounds 3-7–3-10, 3-13–3-16, 5-1–5-10, 6-13–6-16, 9-1–9-16), may increase (compounds 3-7–3-10, 3-13–3-16, 5-1–5-10, 6-13–6-15, 9-2–9-8 and 9-10–9-16) or decrease (compounds 6-15 and 6-16, 9-1 and 9-9) the melting temperatures, and may increase (compounds 3-15 and 3-16, 9-6–9-8 and 9-14–9-16) or decrease (compounds 3-7, 3-9 and 3-10; 3-13 and 3-15, 9-4 and 9-12) the number of mesophases in comparison with the corresponding di-alkyl, alkyl-alkoxy, and alkoxy-alkyl derivatives.

The nematic ranges of di-alkoxy derivatives can be broader (compounds 5-1–5-10, 6-13–6-16, 9-1–9-4 and 9-9–9-12, 9-6 and 9-14) or narrower (compounds 9-5 and 9-13) compared with those of the corresponding di-alkyl, alkyl-alkoxy, and alkoxy-alkyl derivatives. As seen in table 9, increasing the alkoxy and corresponding alkyl chain lengths lowers the clearing points of three-ring derivatives (compounds 9-1–9-16). While for the two-ring derivatives presented in table 5 (compounds 5-1–5-10) the replacement of di-alkoxy by corresponding di-alkyl chains changes the character of the series from descending to ascending. Similar results are seen for non-symmetrical alkoxy-alkoxy derivatives presented in table 8.

The data collated in tables 1 and 4 show that moving the oxygen atom in the terminal groups away from the molecular core can either lower the nematic thermostability and melting points, or have no effect on the isotropic character (compounds 1-1 and 1-11; 1-13 and 1-15; 4-1, 4-3 and 4-4; 4-6 and 4-8; 4-9 and 4-10), in comparison with the corresponding alkoxy derivatives which have the same number of carbon atoms. Further moving of the oxygen in these alkoxyalkyl groups may introduce the nematic phase and increase the melting temperature (which is still lower than that of the corresponding alkoxy derivative, compounds 4-1 and 4-3–4-5) or decrease the thermostability of the monotropic nematic phase and increase the melting point (compounds 4-10–4-12). Interestingly, the insertion of one more oxygen into the alkoxyalkyl group does not change the non-mesomorphic character of the parent alkoxyalkyl derivative (compounds 1-11 and 1-12). The repulsion between neighbouring molecules, with increasing intermolecular separation, may be responsible for these suppressed mesomorphic properties [1]. Similar results have been reported for other alkoxyalkyl derivatives [135–144].

The results presented in this section reveal the importance of the molecular structure to the mesomorphic properties of terminally alkoxy-substituted achiral calamitic LCs. Similar trends have been reported for other alkoxy derivatives [49, 87, 128, 145–155] including

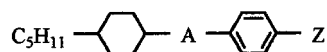
perfluoroalkylalkoxy [156–167], alkoxyalkenyl [168, 169] and cyanoalkoxy derivatives [88, 170–178].

2.2. Linking alkoxy substitution

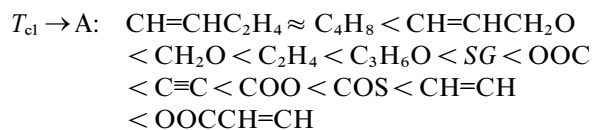
Following the previous discussion on the influence of the alkoxy linkage on mesophase formation in three-ring cyano derivatives, let us consider this effect in more detail. It has been reported that the C–O bond of the methyleneoxy linkage is close to coplanar with the substituted benzene ring. This *trans* geometry makes possible the delocalization of the oxygen lone pair into the electron-deficient aromatic ring [179].

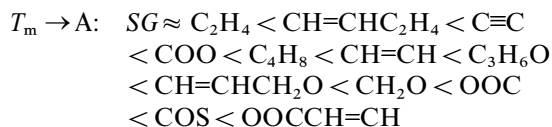
As can be seen from tables 10–15, the introduction of alkoxy groups as linkages into the molecular core of achiral calamitic LCs can increase (compounds 11-5, 11-6 and 11-14) or lower (compounds 10-1, 10-2 and 10-13; 10-14 and 10-15; 12-1, 12-2 and 12-12; 12-5 and 12-11; 14-1, 14-2 and 14-16; 14-8, 14-9 and 14-4; 14-3 and 14-14; 14-5 and 14-15; 15-1 and 15-4; 15-5 and 15-8; 15-9 and 15-12) the clearing points compared with those of the parent compounds. Similarly, the melting temperatures of LCs containing the alkoxy linkages can be higher (compounds 10-1, 10-2 and 10-13; 10-14 and 10-15; 11-6, 11-7 and 11-14; 12-1 and 12-12; 14-1, 14-2 and 14-16; 14-9 and 14-4; 14-3 and 14-14; 15-1 and 15-4) or lower (compounds 12-2 and 12-12; 12-5 and 12-11; 14-4 and 14-8, 14-5 and 14-15; 15-9 and 15-12) than those of the parent compounds. Also, the nematic ranges can be broader (compounds 14-1, 14-2 and 14-16; 14-3 and 14-14; 15-5 and 15-8) or narrower (compounds 10-14 and 10-15, 12-1, 12-2 and 12-12; 12-5 and 12-11; 14-5 and 14-15, 15-1 and 15-4; 15-9 and 15-12). Increasing the length of alkoxy linkages may enhance (compounds 10-1 and 10-2, 11-5 and 11-6) or lower (compounds 12-1 and 12-2, 14-1 and 14-2, 14-8 and 14-9) the clearing temperatures; increase (compounds 11-5 and 11-6, 14-8 and 14-9) or decrease (compounds 10-1 and 10-2, 12-1 and 12-2, 14-1 and 14-2) the melting points; and increase (compounds 14-1 and 14-2) or decrease (compounds 12-1 and 12-2) the nematic ranges. The efficiency of the A linkages introduced into the molecular core of liquid crystalline derivatives can be expressed by the following orders of increasing clearing (T_{cl}) and melting (T_m) temperatures, and nematic ranges (ΔT) (compounds 10-1–10-13; 11-1, 11-5–11-14; 12-1–12-12; 13-1–13-12; 14-1–14-16; 15-1–15-11; tables 10, 11–15):

System (II)

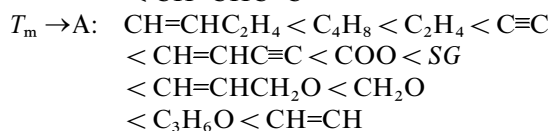
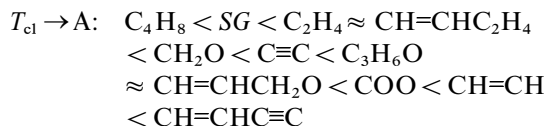


Z is CN

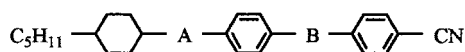




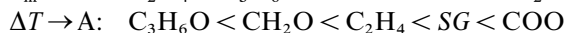
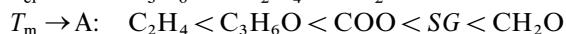
Z is OCH_3



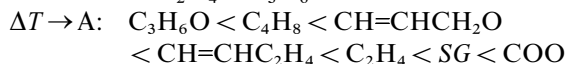
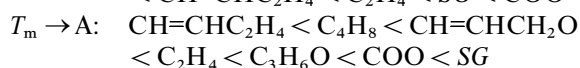
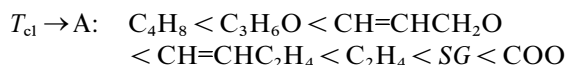
System (III)



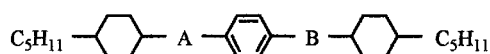
B is SG



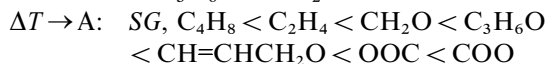
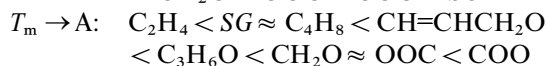
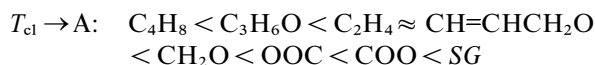
B is COO



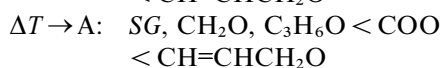
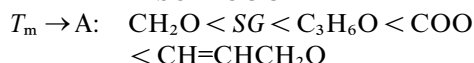
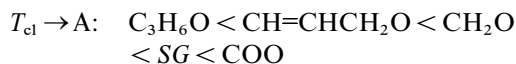
System (IV)



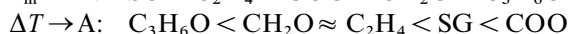
B is SG



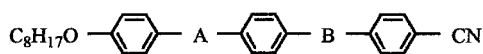
B is C_4H_8



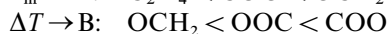
B is OC_3H_6



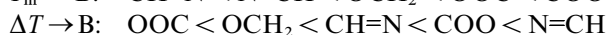
System (V)



A is SG



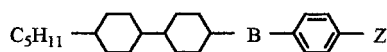
A is OOC



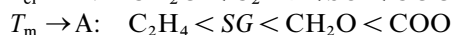
A is N=CH



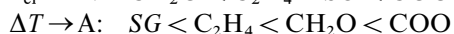
System (VI)



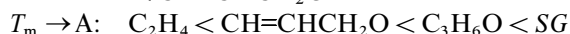
Z is $OCHF_2$



Z is CF_3



Z is F



Keeping in mind that the geometrical and electronic structures of the alkoxy and other linking groups [179, 190–197], play a very important role in the mesomorphic behaviour of liquid crystals, we can point out that, according to the systems (II–VI) presented above, the thermal efficiency of the linkages is strongly dependent on the LC molecular structure. In many cases LCs containing alkoxy linkages exhibit lower clearing temperatures, higher melting points and narrower nematic ranges in comparison with those of corresponding compounds having other linking groups.

In particular, in three-ring octyloxy-substituted cyano derivatives, the introduction of one oxymethylene group into the molecular core results in decreasing nematic

thermostability in comparison with that of the majority of LCs presented in table 13. Also it does not create the modulated smectic C_{mod} phase, unlike the corresponding ester linkage (compounds **13-1** and **13-3**, see also **13-2**, table 13); while the insertion of the oxymethylene and ester or azomethyne groups finally results in the formation of the smectic C_{mod} phase (compounds **13-5** and **13-12**). Interestingly, in the corresponding ester derivatives, this phase disappears (compound **13-6**) or remains (compound **13-12**). As can be seen from table 13, the introduction of the oxymethylene group alone or with other linkages is unfavourable for the reentrant nematic and modulated smectic A_{mod} phases.

The importance of the orientation of alkoxy linkages is clearly shown in table 15 with higher melting and clearing points and narrower nematic range recorded for compound **15-13** (which has the oxygen atom of the methyleneoxy linkage pointed toward the aromatic 4-fluorophenyl fragment), in comparison with those of compound **15-14** with the opposite direction of its oxygen (pointed toward the saturated bi-cyclohexyl fragment). It is believed that for these two compounds only **15-13** exhibits conjugation between the oxygen and the phenylene fragment. This leads to a molecular packing that provides a higher nematic thermostability than that of compound **15-14** (see also [103, 201]).

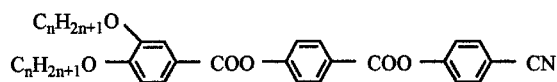
As can be seen from table 14, the introduction of the methyleneoxy and oxypropylene linkages into the LC molecular core (compound **14-12**) gives higher nematic and smectic A thermostabilities and a lower melting point in comparison with those of the corresponding compound **14-13** which contain propyleneoxy and oxypropylene linking groups (see system IV). Similar results have been reported for other liquid crystalline systems having alkoxy linkages [43, 91, 103, 155, 186, 198–223], while the growth of the intramolecular flexibility of linking groups, including the oxyethylene, is responsible for the distortion of the rod-like molecular arrangement and consequent decrease in clearing points [217].

2.3. Lateral alkoxy substitution

As in the case of other lateral substitutions of achiral calamitic liquid crystals [15, 16, 224], alkoxy substitution lowers the clearing temperatures (compounds **16-1** and **16-2**; **16-10**, **16-15**, **17-12**; **6-9**, **16-12**, **17-14**; **16-13**, **16-16**, **17-15**, **18-4**, **18-7**; **16-14**, **16-17**, **17-16**; **17-1**–**17-8**; tables 6, 16–18), and increases (compounds **6-9** and **17-14**; **16-14**, **16-17**, **17-16**; **17-1** and **17-2**) or lowers (compounds **16-1** and **16-2**; **16-10**, **16-15**, **17-12**; **6-9** and **16-12**; **16-13**, **16-16**, **17-15**, **18-4**, **18-7**; **17-1** and **17-3**–**17-8**) the melting points in comparison with those of the corresponding parent compounds. An increase in the quantity of lateral alkoxy substituents further lowers the clearing temperature [236].

The introduction of lateral alkoxy groups can lead to the disappearance of smectic phases (compounds **16-1** and **16-2**; **16-10** and **16-15**; **17-1**–**17-3**; **16-16**, **18-4**, **18-7**) or nematic phases (compounds **16-14**, **16-17**, **17-16**; **17-1** and **17-7**, **17-8**; **6-9** and **17-14**; **16-16** and **17-15**) or reentrant nematic phases (compounds **16-16**, **17-15**, **18-4**, **18-7**; **16-17** and **17-16**). Alkoxy substitution may also introduce the reentrant nematic phase (compounds **6-9** and **16-12**) or result in the disappearance of the smectic A phase and the formation of the smectic C phase (compounds **17-1** and **17-4**–**17-8**). As discussed above for terminally alkoxy-substituted cyano derivatives, the reentrant nematic phase may commence from the octyloxy homologue (compound **16-12**). If this phase once disappears with increasing length of terminal alkoxy chain, it does not reappear in longer homologues (compounds **16-10**–**16-14**). Increasing the length (van der Waals volume) of a lateral alkoxy group can increase (compounds **17-7**, **17-8** and **17-3**–**17-6** and [237–239]) or decrease (compounds **16-10** and **17-12**, **16-12** and **17-14**, **16-13** and **17-15**, **16-14** and **17-16** and [232, 233, 235, 237–241]) the clearing temperatures; and enhance (compounds **16-10** and **17-12**, **16-12** and **17-14**, **16-13** and **17-15**, **17-5**–**17-8**, **17-6** and **17-7**) or lower (compounds **16-14** and **17-16**, **17-2**–**17-4** and **17-5**–**17-8**, **17-7** and **17-8**) the melting points. It has been suggested that an increase in the van der Waals volume of lateral substituents should lower the clearing temperatures of LCs [242, 243]. However, it is difficult to explain some of the presented results in terms of this suggestion, see also [224]. As can be seen from table 17, the simultaneous and equal increase in the lengths of lateral and terminal alkoxy substituents results in the introduction of the smectic A phase starting from the pentyloxy homologue, and the disappearance of the nematic phase from the heptyloxy homologue (compounds **17-9**–**17-16**). The melting and clearing temperatures exhibit more complicated behaviours consistent with the following orders:

System (VII)



$$T_{cl} \rightarrow C_nH_{2n+1}O: \quad C_5H_{11}O < C_6H_{13}O < C_4H_9O \\ \approx C_{10}H_{21}O < C_3H_7O \approx C_9H_{19}O \\ < C_8H_{17}O < C_7H_{15}O$$

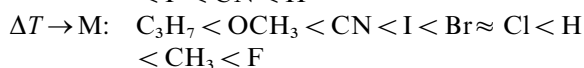
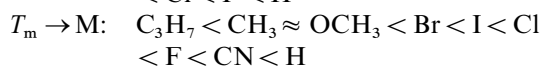
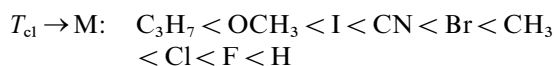
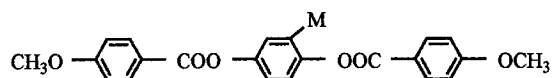
$$T_m \rightarrow C_nH_{2n+1}O: \quad C_9H_{19}O \approx C_{10}H_{21}O < C_8H_{17}O \\ < C_7H_{15}O < C_6H_{13}O < C_4H_9O \\ < C_3H_7O < C_5H_{11}O$$

These results and the data presented in table 17 show that the clearing and melting temperatures reach maximum values at $n = 7$ and $n = 5$, respectively, then fall. It

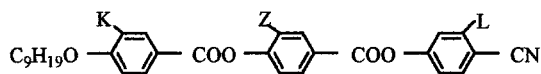
has been demonstrated that further increase in the length and the number of lateral alkoxy groups may lead to the formation of polycatenar mesogens, as discussed in [244].

The mesogenic efficiency of alkoxy and other lateral substituents can be expressed as follows (compounds **16-1-16-9**; **16-13**, **16-16**, **18-1-18-8**; tables 16, 18).

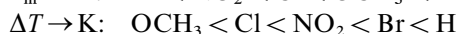
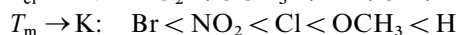
System (VIII)



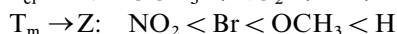
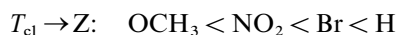
System (IX)



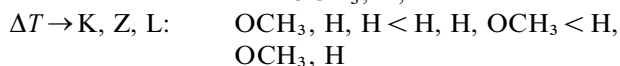
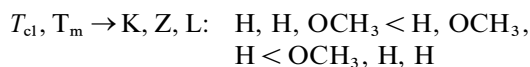
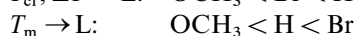
Z, L are H



K, L are H



K, Z are H



These results show that the mesogenic efficiency of lateral methoxy and other groups depends on the structure of the core and their positions in it. In particular, lateral methoxy substitution is less efficient and in many cases gives higher melting temperatures than the corresponding methyl substitution (see also [240, 245, 246]), while propyl substitution results in the lowest clearing and melting temperatures and narrowest nematic range among compounds of the system (VIII). In some three-ring cyano derivatives the replacement of a lateral methoxy

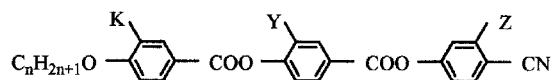
group by methyl can introduce SmA_2 [246] or N_{re} phases [245]. Changing the position of a lateral methoxy group in the phenylene fragment can affect the group's efficiency, and change its decreasing behaviour to an increasing behaviour of the nematic range upon the insertion of lateral methoxy groups (system IX). The introduction of a lateral methoxy group into position K of the system (IX) gives the highest clearing and melting points and narrowest nematic range in comparison with compounds having an OCH_3 group, respectively, in positions Z and L. Similar effects have been found for compounds **17-15** and **18-9** (tables 17, 18) having lateral nonyloxy groups, with lower clearing and melting points recorded for the latter compound. Its depressed mesomorphic properties can be explained in terms of the increased non-linearity (and, consequently less efficient molecular packing) caused by enhanced conjugation between the alkoxy and ester groups, see also [234, 247].

Basically, an increase in the van der Waals volume (length) of the alkoxy group lowers the clearing points of LCs [232, 233, 235, 238-240, 248]. However, there are some contrasting cases [238, 239] which reveal the importance of molecular structure of laterally alkoxy-substituted LCs on their phase transition temperatures.

It has been demonstrated that the introduction of other lateral substituents into the molecular core of laterally alkoxy-substituted LCs further decreases their clearing temperatures [240, 248]. Generally, 4-substitution by polar and weakly polar groups gives higher clearing temperatures than those of the corresponding 2- and 3-substituted LCs [234, 238, 239, 248, 249]. However, the presence of the ethyloxy group at the 3-position of the phenylene fragment gives rise to monotropic nematic thermostability of the 2-methyl substituted compound **17-18** in comparison with the corresponding 4-methyl substituted compound **17-17** (table 17). This unusual behaviour has been interpreted in terms of the conformation effect of the lateral ethyloxy group [235].

The effect of lateral substitution by methoxy and other groups on the appearance of phases between the crystalline and isotropic states in some homologous series of three-ring cyano derivatives can be described by the following system (X):

System (X) [229, 231]



(a) K is OCH_3 , Y, Z are H

$n = 6, 7$ N

$n = 8$ N_{re} , SmA_d , N

$n = 9$ SmA_d , N

$n = 10$ SmA_d

- (b) K is Cl, Y, Z are H
 $n = 7$ SmA_d, N
 $n = 8$ SmA, N_{re}, SmA_d, N
 $n = 9$ SmA_d, N
- (c) (K is Br, Y, Z are H
 $n = 7$ SmA_d, N
 $n = 8$ SmA, N_{re}, SmA_d, N
 $n = 9, 10$ SmA, SmA_d, N
- (d) K is NO₂, Y, Z are H
 $n = 7$ N
 $n = 8-10$ SmA_d, N
- (e) K, Z are H, Y is OCH₃
 $n = 9, 10$ N
 $n = 11, 12$ SmC_d, SmA_d, N
- (f) K, Z are H, Y is Br
 $n = 9-11$ N
 $n = 12$ N_{re}, SmA_d, N
- (g) K, Z are H, Y is NO₂
 $n = 7, 8$ N
 $n = 9$ SmC₂, N
 $n = 10$ SmC₂, SmC_d, SmA_d, N
 $n = 11, 12$ SmC₂, SmC_d, SmA_d
- (h) K, Y are H, Z is OCH₃
 $n = 9-11$ N
- (i) K, Y are H, Z is CH₃
 $n = 11$ N
 $n = 12$ N_{re}, SmA_d, N
- (j) K, Y are H, Z is Br
 $n = 8$ N
 $n = 9-12$ N_{re}, SmA_d, N

These results show that lateral methoxy substitution, depending on its position in the core, may lead to the reentrant nematic phase for a lower homologue and reduce the number of homologues exhibiting this phase in comparison with those of the parent system (Xa, If). Also it may result in the disappearance of the reentrant nematic phase (Xe, Xh, If). The replacement of a lateral methoxy group by other groups may maintain the reentrant nematic phase (Xa, Xb, Xc), introduce this phase (Xe and Xf; Xh and Xi, Xj), or result in its disappearance (Xa, Xd). In some cases lateral methoxy substitution gives more pronounced nematic behaviour compared with other corresponding substitutions (Xe and Xg; Xh and Xj).

Similar trends have been observed for other laterally alkoxy-substituted LCs [250–268] and liquid crystalline derivatives having lateral alkoxy substituted molecular fragments [269, 270].

It seems that there is no direct correlation between the electronic structure of alkoxy and reference groups (characterized by Hammett substituent constants and resonance and field parameters [271]) and the mesomorphic properties of LCs incorporating them. However, the electronic and geometrical structure of the alkoxy groups [179, 190, 272–275] and the corresponding alkyl and other groups [190–196, 272, 276–278] play a very important role in the intra- [279, 280–293] and inter-molecular [21–32, 279, 280, 291, 294–296] interactions affecting molecular packing which predominantly influences mesophase thermostability [291, 293–297]. Anisotropic dispersion interactions, and consequently the anisotropy of polarizability, which depend 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 steric factors [297]. Other molecular aspects, such as association [293] or dipole–dipole attraction in polar liquid crystalline derivatives, that influence the packing of the molecules also affect the stability of the mesophases [297].

2.4. X-ray data

It has been shown that X-ray diffraction (XRD) of LCs is a useful method for the study of the effects of the association of LC molecules on the structure of their mesophases [34, 36, 37, 298, 299]. The investigation of polar LCs 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 with period d . They involve swarms containing tens to hundreds of molecules and are characterized by a correlation length ξ defined directly from the width of the diffraction peak. For the nematic phase of some two-ring cyano derivatives it has been shown that the ratio d/L , where L is the molecular length, is about 1.2–1.5 [34, 36, 37, 298, 299]. 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 different chemical classes, showed that d depends on the molecular structure of the polar LCs and characterizes in particular the degree of overlap of the molecular cores on dimer formation. Further XRD investigations of the nematic phase of polar LCs showed in some cases the simultaneous existence of two fluctuation layer structures with incommensurate periods d_1 and d_2 , where $d_1 < L < d_2 < 2L$ [34, 36, 298, 299].

XRD studies of 4-alkoxy-4'-cyanobiphenyls failed to reveal the simultaneous existence of two fluctuation layer

structures with incommensurate periods {compounds **1-2**, **1-3**, **1-5**, table 1 and [34, 300]}. For the corresponding alkyl derivatives the situation concerning two fluctuation layer structures is unclear [36, 38]. It may also be important to consider the ratio d/L which is greater than 1 for two-ring cyano and nitro-substituted alkoxy derivatives (compounds **1-2**, **1-3**, **1-7**, table 1 and [34, 301–304]). However, it is difficult to analyse these data, since the measuring temperature was not mentioned in many cases for the corresponding 4-*n*-alkoxy- and 4-*n*-alkyl-4'-cyanobiphenyls. On other hand, a higher molecular overlapping has been proposed for the alkoxy-substituted cyanobiphenyls than for the corresponding alkyl-substituted derivatives [291]. This situation looks more clear for three-ring alkoxy and the corresponding alkyl-substituted cyano derivatives having ester linkages with a lower ratio d/L (higher molecular overlap) in the nematic [86, 305] and smectic A_d phase of the former derivative [306, 307]. 4-Pentyloxy-4''-cyano-*p*-terphenyl **1-13** exhibits only one dimeric density wave in comparison with the dimeric and monomeric density waves observed in the corresponding pentyl derivative **1-14** (table 1).

Terminally alkoxy-substituted two-ring liquid crystalline derivatives of low polarity usually exhibit monolayer formation ($d/L \leq 1$) of their mesophases, which in some cases is similar to monolayer organization of the mesophases of the corresponding alkyl derivatives {compounds **5-1-5-5**, **5-8-5-10**; **8-3-8-8**, **8-11-8-16**; tables 5, 8 and [302, 308–323]}. Similar increasing temperature dependences of the layer spacing for the corresponding compounds **8-3-8-8** and **8-11-8-16** [87] have been demonstrated. Changing the orientation of the ester linkages and/or the length of alkoxy(alkyl) chains may significantly affect these dependences, leading in some cases to a large difference in the temperature behaviour of the layer spacing between corresponding alkoxy and alkyl derivatives [87].

Surprisingly, a dimeric density wave with period d_2 has been recorded for some weakly polar derivatives {compound **11-1**, table 11 and [96, 324, 325]}. A comparison of the values of d_2/L of compounds **11-1** and **10-9** (tables 10, 11) reveals that replacement of the methoxy group by cyano increases the degree of molecular overlap in the formation of the dimers.

As can be seen from table 10, the introduction of the methyleneoxy linkage into the molecular core of compound **10-15** to produce compound **10-14** maintains the existence only of a dimeric density wave with decreased level of molecular overlapping in the dimers. Similar results have been reported for three-ring cyano derivatives incorporating oxymethylene and ester linkages, with a higher molecular overlap in the dimers recorded for the latter compounds [306, 326].

It can be seen from table 17 that lateral alkoxy substitution of three-ring cyano derivatives leads to the disappearance of the dimeric smectic A phase and to the formation of a monolayer smectic C phase (compounds **17-1** and **17-5–17-8**). Lateral methoxy substitution of 4-cyanophenyl 4-(4-nonyloxybenzoyloxy)benzoate results in increasing molecular overlapping in dimer formation in comparison with the parent compound and the corresponding Cl and Br derivatives (compounds **16-13**, **16-16**, **18-1–18-3**, table 18):

$$d/L \rightarrow K: \text{OCH}_3 \approx \text{NO}_2 < \text{Cl} < \text{H} < \text{Br}$$

It has been reported that the replacement of a lateral methoxy group by methyl increases the layer spacing and decreases the average rate of thermal expansion of the layers in some three-ring cyano derivatives [246]. Similar trends have been demonstrated for other liquid crystalline derivatives having terminal alkoxy groups [34, 35, 66, 76, 81, 96, 291, 301–304, 306, 308–323, 325, 327–372], laterally alkoxy substituted groups [245, 246, 258], and alkoxy linkages [213, 326, 373–376].

3. Static dielectric properties

The relationship between the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where ε_{\parallel} and ε_{\perp} are, respectively, dielectric constants, that are parallel and perpendicular to the nematic director \mathbf{n}) and LC molecular structure is described by the theory of Maier and Meier [377]:

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

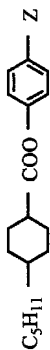
where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$, and $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the polarizability anisotropy. F is the cavity reaction field, μ is the dipole moment, β is the angle between the molecular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

It has been shown that meaningful comparisons of the dielectric properties of LCs with different nematic–isotropic phase transition temperatures T_{N-I} can only be made at constant reduced temperature $\tau = T_{\text{meas}}/T_{N-I}$ [378]. Tables 5, 15, 18 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 [378], the extrapolations are not meaningful, however these estimations are the only way to obtain a rough definition of the dielectric properties of non-mesomorphic compounds, smectic LCs, and LCs with a narrow nematic range.

Data on the dielectric properties of some cyano derivatives and their binary mixtures presented in table 19 demonstrate that the replacement of an alkoxy group by

Table 19. Physico-chemical and electro-optical (d -cell gap = 10 μm , $U = 3$ V) properties of liquid crystals [9, 46, 101, 102, 386, 417–427]. For compositions see below.

Compound	μ^a/D	ϵ_L^b	$\Delta\epsilon^b$	$\Delta\epsilon/\epsilon_L^b$	g, T_{N-1}	$n_o^{d,e}$	$\Delta n^{d,e}$	K_{11}^h/pN	K_{33}/K_{11}^h	η/cSt	γ_1^a/P	E/eV	k_p^1	U_{90}/V	U_{10}/V	$\tau_{on1}/(ms)$	$\tau_{on2}/(ms)$	$\tau_{off}/(ms)$
1-2	5.2	8.2	8.5	1.04	0.47	1.528	0.176	4.9	1.18	25 ⁱ			0.6226					
1-7	4.8	6.8	10.3	1.52	0.53	1.528	0.185	6.2	1.33	25 ⁱ			0.6292					
19-1		6.5 ^c	10.1 ^c	1.55 ^c			0.177 ^c	6.1 ^c	1.25 ^c		3.3 ^k	0.517		1.51 ^a	2.26 ^a	375 ^a	125 ^a	125 ^a
19-2		6.0 ^c	11.7 ^c	1.95 ^c			0.184 ^c	8.0 ^c	1.36 ^c		1.1	0.546		1.30 ^a	1.78 ^a	85 ^a	21 ^a	69 ^a
11-1	2.0	4.2 ^c	-0.9 ^c	-0.21 ^c	0.98	1.474 ^c	0.062 ^{c,f}	6.8 ^c	1.21 ^c				0.6010 ^m					
11-2	1.6		-0.4		0.90			5.1 ^b	1.06 ^b									
10-9	4.9		7.3 ^c		0.54		0.092 ^{c,f}	6.0 ^c	1.68 ^c									



1-2 Y = C₅H₁₁O; **1-7** Y = C₅H₁₁

19-1 Mixture (C₅H₁₁O and C₇H₁₅O = 40:60 mol %)

19-2 Mixture (C₅H₁₁ and C₇H₁₅ = 40:60 mol %)

^a $T_{meas} = 25^\circ\text{C}$.

^b $\tau = 0.98$.

^c $\tau = 0.95$.

^d $\lambda = 632.8$ nm.

^e $\tau = 0.96$.

^f $\lambda = 589.3$ nm.

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

ⁱ $T_{meas} = 47.9^\circ\text{C}$.

^j $T_{meas} = 28.3^\circ\text{C}$.

^k Extrapolated to $T_{meas} = 25^\circ\text{C}$.

^l $T_{meas} = 85^\circ\text{C}$.

^m $T_{meas} = 50^\circ\text{C}$.

the corresponding alkyl group increases (compounds **1-2** and **1-7**, mixtures **19-1** and **19-2** and [379]) or decreases [47] the dielectric anisotropy. Basically, terminally alkoxy-substituted compounds exhibit higher values of the dipole moments than those of the corresponding alkyl compounds {compounds **1-2** and **1-7**, **5-1-5-4** and **5-6-5-9**, **11-1** and **11-2** and [107]}. In particular, substitution of the benzene by the methoxy group increases its dipole moment to 1.28 D and gives an angle of 72° between the dipole and the *pp*-axis [107]. The corresponding toluene shows a dipole of 0.37 D and an angle of 0° [107]. For the alkoxy group, which rotates freely, the angle between the *pp*-axis and the long molecular axis is about 10° [67]. Thus one can expect a large contribution to ϵ_{\perp} from its additional dipole moment in comparison with that of the alkyl group (compounds **1-2** and **1-7**, **5-1-5-4** and **5-6-5-9**, tables 5, 19). The constant ϵ_{\parallel} can also be influenced because of the absence of compensation between the dipole moments of the alkyl group and the parallel part of the alkoxy dipole, and because of conjugation between the electrons of the oxygen and the molecular core which can enhance α_{\parallel} (see § 1) [67]. In the case of weakly polar compounds the increase of ϵ_{\perp} dominates over that of ϵ_{\parallel} resulting in increasing (in absolute value) the negative dielectric anisotropy (compounds **8-8**, **11-1** and **11-2**, tables 8, 19) or changing the sign of $\Delta\epsilon$ from positive to negative in alkoxy [43] and dialkoxy derivatives (compounds **5-1-5-4** and **5-6-5-9**, table 5 and [67]). A change of orientation of ester linkages in compound **8-8** may change the sign of its negative dielectric anisotropy [88]. A similar increase of ϵ_{\perp} and an additional decrease of the molecular packing—see equation (1)—may be responsible for lower values of the dielectric anisotropy recorded for two-ring alkoxy-substituted cyano derivatives compared with those of the corresponding alkyl compounds (compounds **1-2** and **1-7**, mixtures **19-1** and **19-2**, table 19 and [379]). Replacement of the methoxy group by cyano leads to a high positive dielectric anisotropy because of increase in dipole moment and polarizability anisotropy (compounds **11-1** and **10-9**, table 19).

As can be seen from table 15, introduction of the methyleneoxy linkage into the molecular core of LCs gives a lower value of $\Delta\epsilon$ due to the dipole moment and polarizability anisotropy being decreased (compounds **15-1** and **15-2**, see also **15-3**, **15-4**). These results are found to be in agreement with equation (1) [377]. Similar trends have been observed for other liquid crystalline alkoxy derivatives [10, 43, 67–69, 88, 103, 234, 245, 246, 380–402].

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 [295, 403–405], but antiparallel association predominates

and reduces the effective dipole moment [293]:

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

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

where $\epsilon_i^{\infty} = 1.05n_i^2$; g is the correlation factor characterizing the association tendency. For non-associating systems g is equal to 1. The value of g for compound **1-2** has been calculated using the reference data. Keeping in mind that the dipole moment of the alkyl- and alkoxy-benzenes is almost the same [406], we can consider in first approximation that the dipole moments of 4-*n*-alkoxy-4'-cyanobiphenyls are equal to 5.2 D [170], see also a similar approximation for *pp'*-di-*n*-alkylazoxybenzenes [64]. The data collated in table 19 reveal that all the compounds under investigation exhibit the g values smaller than 1, indicating an antiparallel association. Replacement of the alkoxy group by alkyl increases (strong polar compounds **1-2** and **1-7**, table 19) or decreases (weakly polar compounds **11-1** and **11-2**, table 19) the factor g . Furthermore, it has been reported that the dimers of alkoxy-substituted cyanobiphenyls are more stable than those of the corresponding alkyl derivatives [407]. Similarly, weakly polar *pp'*-di-*n*-alkoxyazoxybenzenes and the corresponding *pp'*-di-*n*-alkylazoxybenzenes show the g values < 1 with more pronounced antiparallel association observed for the latter derivatives (compounds **5-1-5-4** and **5-6-5-9**, table 5).

These results show that the association tendency of alkoxy derivatives is strongly influenced by their molecular structures, see also [408, 409].

4. Optical properties

The phenomenological relation between refractive index and electric polarization is defined as [410, 411]:

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

where the mean polarizability $\alpha^* = (\alpha_{\parallel} + 2\alpha_{\perp})/3$; the mean refractive index $n^{*2} = (n_e^2 + 2n_o^2)/3$; n_o is the ordinary and n_e the extraordinary refractive indices. From equation (4) and the previous section, it follows that the cyano derivative, which has a large induced polarizability from the highly conjugated π -electron system, exhibits an optical anisotropy $\Delta n = n_e - n_o$ much larger than that of the corresponding alkoxy derivative (compounds **11-1** and **10-9**, table 19 and [101, 102]). The increased values of anisotropy of polarizability recorded for alkoxy derivatives should lead to higher optical anisotropies than those of the corresponding alkyl derivatives [101, 102, 412, 413]. However, some

opposite cases have been reported [101, 102, 412] that can be realized within the same homologous series by decreasing the alkoxy(alkyl) chain length [412].

In the case of di-alkoxy and the corresponding di-alkyl derivatives, the increased values of Δn correspond to increased values of the anisotropy of polarizability which have been observed for the former derivatives [71] (compounds **5-1-5-5** and **5-6-5-10**, table 5). These effects can be explained in terms of the reduction or extension in effective conjugation length of the π -electron system, resulting in a shorter or longer resonance wavelength of the UV absorption spectrum for the alkoxy-substituted derivatives in comparison with the corresponding cyano and alkyl derivatives, respectively [414]. However, in the case of the alkoxy- and alkyl-substituted cyanobiphenyls, the UV data is not supported by the measurements of the optical anisotropy: lower values have been recorded for alkoxy derivatives which show a longer electronic resonance wavelength than those of the corresponding alkyl derivatives (compounds **1-2** and **1-7**, mixtures **19-1** and **19-2**, table 19 and [414–416]). Again, these and the earlier discussed results can be explained in terms of looser molecular packing of the alkoxy-substituted derivatives compared with that of the corresponding alkyl derivatives (compounds **1-2** and **1-7**, table 19 and [415]).

The data presented in table 15 show that the introduction of the methyleneoxy linking group into the LC molecular core lowers the optical anisotropy; this can be attributed to the reduced conjugation length of the π -electron system compared with that of the parent and corresponding compounds with other linkages (compounds **15-1** and **15-3, 15-4**).

Similar trends have been demonstrated for other alkoxy derivatives [10, 43, 70, 71, 101, 103, 170, 343, 390, 401, 409, 412, 428–463].

5. Visco-elastic properties

It has been shown that nematic liquid crystalline materials for display applications need a low viscosity to give acceptable LCD response times [378, 464]. The rotational viscosity γ_1 of a nematic liquid crystal (NLC) is a dissipative coefficient describing the rate of reorientation of the NLC director [465]. The magnitude of the rotational and flow viscosities depend on molecular structure, intermolecular association, and temperature [466, 467]: as temperature increases, viscosity decreases [65, 72, 421, 466, 467].

According to the results on flow viscosity η and rotational viscosity γ_1 presented in tables 5, 19, the alkoxy- and di-alkoxy-substituted derivatives exhibit higher values of flow and rotational viscosity compared with the corresponding alkyl and di-alkyl derivatives (compounds **5-1-5-4** and **5-6-5-9, 1-2** and **1-7**, mixtures

19-1 and **19-2** and [134, 467–469]). Also, the replacement of terminal alkoxy groups by cyano increases the viscosity [134, 467–469], which can be explained in terms of the increased association tendency (compare values of g for compounds **11-1** and **10-9**, table 19 and [470]). In particular, compounds **1-2** and **1-7, 5-1-5-4** and **5-6-5-9** exhibit similar viscosity values but for the corresponding alkoxy and di-alkoxy derivatives they have been measured at significantly higher temperatures. A more pronounced and stable association tendency of alkoxy-substituted cyanobiphenyls in comparison with the corresponding alkyl derivatives (see §3) may be responsible for increasing the viscosity (compounds **1-2** and **1-7**, mixtures **19-1** and **19-2**, and [421, 470]). Similar results have been obtained for other alkoxy derivatives [10, 72, 390, 401, 402, 421, 467, 471–487].

In the bulk of NLCs elastic properties are determined by three elastic constants (Oseen–Frank constants), corresponding to the restoring forces opposing splay (K_{11}), twist (K_{22}), and bend (K_{33}). The distortion-free energy density is [73, 488, 489]:

$$F = 1/2[K_{11}(\nabla \cdot n)^2 + K_{22}(n \cdot \nabla \times n)^2 + K_{33}(n \cdot \nabla n)^2]. \quad (5)$$

It has been shown that the elastic constants depend on molecular structure, intermolecular association, and temperature of NLCs [65, 73, 490]. One example of these dependences is presented in table 19 where the alkoxy-substituted cyanobiphenyls exhibit lower values of K_{11} and K_{33} compared with those of the corresponding alkyl derivatives (compounds **1-2** and **1-7**, mixtures **19-1** and **19-2**, see also [379]). The replacement of the cyano group by methoxy in compound **10-9** to obtain compound **11-1** results in an increase in K_{11} and a decrease in K_{33} .

The elastic constant ratio K_{33}/K_{11} of liquid crystalline materials is a very important parameter for super twisted nematic liquid crystal displays (STN-LCDs), defining their electro-optical performance [491].

As can be seen from table 19, alkoxy-substituted cyanobiphenyls show lower values of the ratio K_{33}/K_{11} than the corresponding alkyl derivatives (compounds **1-2** and **1-7**, mixtures **19-1** and **19-2**). It has been shown that elastic constant ratio K_{33}/K_{11} is a linear function of the squared dimeric density wave period d_2^2 for binary mixtures of two-ring alkyl-substituted cyano derivatives [36]. 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, it may be proposed that for fifth and longer homologues of two-ring alkoxy- and alkyl-substituted cyano derivatives the balance in the monomer–dimer system $2M \leftrightarrow D$ (considering data

on the correlation factor g in table 19 and on the correlation lengths ζ in [36, 298]) is biased towards dimers defining the LC properties [36, 492, 493].

It can also be seen from table 19 that replacement of the methoxy group by methyl or cyano in the weakly polar compound **11-1** decreases (compound **11-2**) or increases (compound **10-9**) the elastic constant ratio. The opposite situation has been observed for the corresponding methoxy (compound **11-1**) and cyano (compound **10-9**) derivatives at temperatures close to the clearing point [494]. From table 5, it can be seen that an increase in the length of terminal alkoxy(alkyl) groups in compounds **5-1-5-5** (**5-6-5-10**) lowers the elastic constant ratio and makes K_{33} less than K_{11} . This has been explained in terms of changing the correlation length (characterizing the tendency to form the smectic phases) parallel and perpendicular to the director, with a more pronounced increase in the latter direction [73].

Considering the data on the correlation factor g , and the more pronounced development of the monomeric density wave, it may be proposed that in the weakly polar di-alkoxy(alkyl) derivatives **5-1-5-10** the balance in the monomer–dimer system $2M \leftrightarrow D$ is biased towards monomers, thus defining their liquid crystal properties. Interestingly, weakly polar di-alkoxy derivatives can exhibit higher (compounds **5-1-5-3** and **5-6-5-8**, table 5) or lower values (compounds **5-4** and **5-9**) of the ratio K_{33}/K_{11} compared with those of the corresponding di-alkyl derivatives. These results show the importance of molecular structure of the alkoxy derivatives on their elastic properties, see also [10, 73, 384, 390, 422, 473, 479, 490, 494–498].

6. Molecular packing

It has been shown that LC molecular packing plays a very important role in the creation of their mesophases [294, 296] and defines their optical properties [410]. The molecular packing coefficient is expressed in [419] as:

$$k_p = N_A V \rho / M, \quad (6)$$

where N_A is the Avogadro number, ρ is the density, M is the molecular mass, and 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 [499].

From table 19 it can be seen that replacement of alkoxy groups by the corresponding alkyl groups in cyanobiphenyls results in an increase in their molecular packing coefficient (compounds **1-2** and **1-7**). A similar replacement by the cyano group in weakly polar compound **11-1** creates the strongly polar compound **10-9** with an increased value of k_p . Similar results have

been demonstrated for di-alkoxy (compounds **5-1-5-5**) and the corresponding di-alkyl (compounds **5-6-5-10**) derivatives presented in table 5 (keeping in mind that the density of nematics decreases with increasing temperature [70, 74]).

These results may be associated with the difference in energy of intermolecular interactions—and therefore with the difference in activation energy of the rotational viscosity of these compounds (mixtures **19-1** and **19-2**, table 19 and [419]). Similar trends have been reported for other alkoxy derivatives [70, 101, 343, 348, 412, 429, 430, 432, 434–438, 444, 446–449, 451, 453, 456, 461–463, 474, 500–520].

7. Comparative characteristics of liquid crystals

Selection of the best components for liquid crystalline materials, and prediction of new chemical structures require comprehensive comparative investigation 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 [384]. This fact is employed for the comparison of physico-chemical properties of liquid crystalline alkoxy- and the corresponding alkyl-substituted cyano derivatives (mixtures **19-1** and **19-2**, table 19, see also [379, 469]). This was done by using binary mixtures (containing a pentyloxy, a heptyloxy, a pentyl and a heptyl homologue) giving broad nematic ranges (mixture **19-1**: $<30-72^\circ\text{C}$, and mixture **19-2**: $<0-39^\circ\text{C}$ [46, 472]) with clearing points depending on the molecular structure as observed for the pure compounds in §2.1.

Table 19 shows that alkoxy-substituted cyanobiphenyls exhibit lower values (compounds **1-2** and **1-7**, mixtures **19-1** and **19-2**) of the ratio $\Delta\epsilon/\epsilon_\perp$, which is favourable for supertwisted nematic display applications [378]. These compounds show higher threshold U_{90} and saturation U_{10} voltages and higher twist-effect response times in comparison with those of the corresponding alkyl derivatives. These findings are consistent with a higher viscosity observed for the alkoxy-substituted cyanobiphenyls and with the dependence of the threshold voltage of the twist-effect on the dielectric anisotropy and elastic constants [378]:

$$U_{90} \propto \pi[\kappa/\epsilon_0 \Delta\epsilon]^{1/2} \quad (7)$$

where κ is the elastic expression, $\kappa = [K_{11} + (K_{33} - 2K_{22})/4]$.

8. Conclusions

The effects of alkoxylation on the physico-chemical properties of achiral calamitic liquid crystals have been studied and some general trends identified and explained.

It is believed that the results of this study will broaden our understanding of fundamental structure–property relationships in liquid crystals.

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