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Nitro substitution in achiral calamitic liquid crystals

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Nitro substitution in achiral calamitic liquid crystals

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This review examines in some detail the effect of terminal and lateral nitro substitutions in achiral calamitic liquid crystals on their physico-chemical properties. The results of this study are compared with those obtained for other groups, and are rationalized in terms of existing theories.

1. Introduction

For many years nitrogen and oxygen atoms have been used as important structural elements in the molecular design of liquid crystals for display applications [1–12]. One nitrogen and two oxygen atoms form the nitro group—one of the most important substituents of organic molecules [13–15]. The attachment of the nitro group to a hydrocarbon of any type significantly changes the electron affinity of the molecule [14–21]. Particularly, the nitrobenzenes form the paradigm of quinoidic mesomerism through the M effect (especially in the case of *para*- and *ortho*-π-donors) and for the explanation of aromatic substitution reactions [13, 15]. The strong mesomeric effect of the nitro group [14] induces a positive charge on the nitrogen atom and increases the electronegativity of the group [15]. The mesomeric interaction with the other part of the molecule is basically reduced simultaneously and only appears in the case of strong electron-donation which leads to through-resonance structures of the quinoidic type in the case of *p*-substituted aryls [15]. This approach of through-resonance has been supported by dipole moment measurements [22] and ^{15}N- and ^{17}O-NMR chemical shift measurements [23, 24]. It has been shown that the electron-withdrawing character of the NO_2 group, which is characterized by means of Hammett constants [25], σ_m and σ_p, is mainly due to induction (I effect) [26]. The low π-mesomerism of nitrobenzene has been explained in terms of the low torsional barrier [17] and large torsional amplitude [17, 21] of internal rotation. This suggestion has been supported by the experimental density distribution [18] and *ab initio* calculations [19, 20].

Here, we would like to study the effect of terminal and lateral nitro substitution in achiral calamitic liquid crystals on their physico-chemical properties. The results of this study will be reviewed, rationalized in terms of existing theories, and compared with those of other well-known substituent groups.

2. Mesomorphic properties

2.1. *Thermal and general data*

Many attempts have been made to understand such factors as the electronic and geometrical parameters of molecular substituents influencing mesophase behavior [1–4, 27–33]. However, the prediction and rationalization of the mesomorphic properties of liquid crystals still remain difficult problems [2, 3, 5, 27, 34–58]. The aim of this paper is therefore to define what relations can be established for terminally and laterally nitro substituted liquid crystals, even though these relationships may be empirical.

The phase transition temperatures of some nitro substituted derivatives and corresponding reference compounds are summarized in tables 1–11 where Cr, SmH, SmG, SmF, SmE, SmB, SmC, SmC$_1$, SmC$_2$, SmC$_{mod}$, SmA, SmA$_1$, SmA$_2$, SmA$_d$, SmA$_{mod}$, SmA$_{dre}$, N$_{re}$, N and I mean the crystalline, smectic H, G, F, E, B, C, C$_1$, C$_2$, modulated C, A, A$_1$, A$_2$, A$_d$, modulated A, reentrant A$_d$, reentrant nematic, nematic and isotropic phases, respectively.

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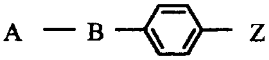
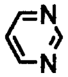
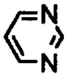
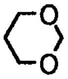
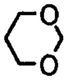
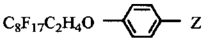
Table 1. Mesomorphic properties of liquid crystals: 

Compound	*A*	*B*	*Z*	Phase transitions/°C	Ref.
1-1	$C_8F_{17}C_2H_4O$	—	NO_2	Cr 49 SmA 78 I	[59]
1-2	$C_8F_{17}C_2H_4O$	—	CN	Cr 56 SmB (42) SmA 81 I	[59]
1-3	$C_8F_{17}C_2H_4O$	—	NH_2	Cr 81 SmB (73) SmA 85 I	[64]
1-4	$C_8F_{17}C_2H_4O$	—	Cl	Cr 73 I	[64]
1-5	$C_8F_{17}C_2H_4O$	—	OCH_3	Cr 61 SmA (52) I	[64]
1-6	$C_8F_{17}C_2H_4O$	—	CH_3	Cr 57 I	[64]
1-7	C_5H_{11}		NO_2	Cr 46 I	[65]
1-8	C_5H_{11}		CN	Cr 30.9 N 47 I	[66]
1-9	C_6H_{13}		NO_2	Cr 111.5 SmC (100.5) I	[67]
1-10	C_6H_{13}		CN	Cr 54.5 N (38.5) I	[68]
1-11	C_7H_{15}		NO_2	Cr 46.5 I	[69]
1-12	C_7H_{15}		CN	Cr 28.5 N 42 I	[70]
1-13	$C_7H_{15}O$		NO_2	Cr 36.5 Sm (30.5) N (38.5) I	[70]
1-14	$C_7H_{15}O$		CN	Cr 53.5 N 75 I	[70]
1-15	C_6H_{13}		NO_2	Cr 56 I	[71]
1-16	C_6H_{13}		CN	Cr 48 N (42) I	[71]

2.1.1. *Terminal nitro substitution*

It has been shown that for one-ring nitro substituted derivatives mesomorphic properties can be observed in 4-, 2-, and 3-perfluoroalkyl substituted nitrobenzenes (compound **1-1**, table 1 and [59–63]). The thermal efficiency of the substituent *Z* of one-ring benzene derivatives (compounds **1-1**–**1-6**, table 1) can be expressed by the following orders of increasing clearing temperatures T_{cl} (smectic–isotropic phase transition temperatures):



(I) *System (I)*

$$T_{cl} \rightarrow Z\colon CH_3, Cl < OCH_3 < NO_2 < CN < NH_2.$$

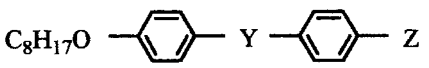
This order differs significantly from the order of efficiency of terminal groups which has been proposed in [2]: $Cl < NO_2 < OCH_3 < CN$, while the melting temperatures T_m (crystal–smectic or crystal–isotropic phase transition temperatures) of system (I) compounds are consistent with the following order:

$$T_m \rightarrow Z\colon NO_2 < CN < CH_3 < OCH_3 < Cl < NH_2.$$

It has been reported that the mesomorphic behaviour of one-ring perfluoroalkyl substituted nitrobenzene derivatives strongly depends on the position of the nitro groups [59–63].

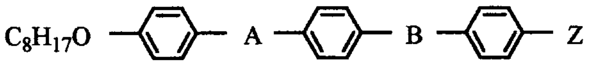
In the case of two- and three-ring derivatives, neither 4-nitrobiphenyl nor 4-nitroterphenyl are mesomorphic [72, 73]. It is evident from tables 1, 2 that the terminal nitro substitution of two-ring derivatives, depending on their structures, does not create mesophases (compounds **1-7**, **1-11**, **1-15**) nor promote the formation of mesophases (compounds **1-9**, **1-13**, **2-1**, **2-3**, **2-5**, **2-7**, **2-9**). The

Table 2. Mesomorphic properties of liquid crystals:



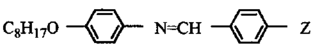
Compound	*Y*	*Z*	Phase transitions/°C	*d*/Å	*d*/*L*	Ref.
2-1	COO	NO_2	Cr_2 47.5 Cr_1 50.4 SmA 61.4 N 68.1 I	29.0	1.14	[74, 75]
2-2	COO	CN	Cr 75.6 N 88 I			[76]
2-3	OOC	NO_2	Cr 64 SmA 71 N 73.2 I			[77]
2-4	OOC	CN	Cr 69 SmC (51) SmA 87 N 93 I			[78]
2-5	N=N	NO_2	Cr 91 SmA 99 N 100 I			[79]
2-6	N=N	CN	Cr 104.5 N 113 I			[80]
2-7	CH=N	NO_2	Cr 92.1 SmA (83.4) N (85.8) I	29.0	1.11	[81]
2-8	CH=N	CN	Cr 79 N 97 I			[82]
2-9	N=CH	NO_2	Cr 63.4 Sm 76.2 N 85.4 I	31.9	1.26	[83]
2-10	N=CH	CN	Cr_2 66.8 Cr_1 73.9 SmA 83.1 N 109 I	36.7	1.39	[83, 84]
2-11	N=CH	H	Cr 69.6 I			[83]
2-12	N=CH	F	Cr 87.4 I			[83]
2-13	N=CH	Cl	Cr 90.2 SmB 97.3 N 108.3 I			[83]
2-14	N=CH	Br	Cr 92.4 SmB 111.7 N 115.1 I			[83]
2-15	N=CH	OCF_3	Cr 84.4 SmA 98.8 I			[85]
2-16	N=CH	CF_3	Cr 96.5 SmB 100.1 I			[85]

Table 3. Mesomorphic properties of liquid crystals:



Compound	*A*	*B*	*Z*	Phase transitions/°C	Ref.
3-1	COO	OOC	H	Cr 117 N 142 I	[87]
3-2	COO	OOC	NO_2	Cr 165 SmA 239 N 246 I	[29, 88]
3-3	COO	OOC	CN	Cr 140 SmA 193 N 255 I	[89]
3-4	COO	OOC	F	Cr 122 N 193 I	[29, 88]
3-5	COO	OOC	Cl	Cr 168 N 217 I	[29, 88]
3-6	COO	OOC	Br	Cr 175 N 217 I	[29, 88]
3-7	COO	OOC	CF_3	Cr 190 SmA 212 I	[88]
3-8	COO	OOC	OCF_3	Cr 149 SmA 203 N 209 I	[88]
3-9	COO	OOC	CH_3	Cr 102 N 199 I	[29, 88]
3-10	COO	OOC	OCH_3	Cr 124 N 224 I	[29, 88]
3-11	—	COO	NO_2	Cr 105 SmA_d 198 N 213 I	[30]
3-12	—	COO	CN	Cr 114 N 227.5 I	[90]
3-13	—	OOC	NO_2	Cr 123.5 SmA_d 197 N 221 I	[91]
3-14	—	OOC	CN	Cr 128 SmC_{mod} (123) SmA_1 159 N 236 I	[91]
3-15	—	OCH_2	NO_2	Cr 108 SmG 114 N_{re} 124 SmA 154 N 162 I	[91]
3-16	—	OCH_2	CN	Cr 129 SmG (119) N 171 I	[91]

efficiency of the terminal groups is consistent with the following orders (compounds **2-9**–**2-16**, table 2), where T_{cl} are the nematic–isotropic or smectic–isotropic phase transition temperatures, and the melting temperatures T_m are crystal–nematic or crystal–smectic or crystal–isotropic phase transition temperatures:



(II) [83, 85] *System (II)*

$$T_{cl} \rightarrow Z\text{: H, F, }OCH_3, CH_3 < NO_2 < OCF_3 < CF_3 < Cl < CN < Br$$

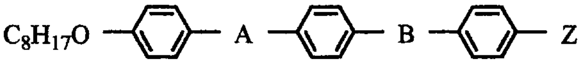
$$T_m \rightarrow Z\text{: }NO_2 < CN < H < CH_3 < OCF_3 < F < Cl < Br < CF_3 < OCH_3,$$

Again, we see the difference between this order of clearing points and that proposed in [2]. Neither do these results, particularly the highest nematic thermostability of the bromine derivative, support the suggestion that the clearing temperature is proportional to the anisotropy of polarizability of compounds having the following terminal substituents *Z* [28, 86]:

$$T_{cl} \rightarrow Z\text{: F} < CH_3 < Cl < Br < NO_2 < CN.$$

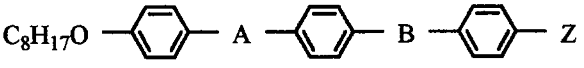
Similar results have been found for the three-ring derivatives presented in tables 3–7. In the mean time, the ester linking groups can be considered as very useful structural elements for the promotion of mesomorphism (compare compound **7-1** (table 7) with non-mesomorphic 4-nitroterphenyl [73]). Moreover, changing the orientations of the ester groups and/or replacing them by other linkages, including a single carbon–carbon bond,

Table 4. Mesomorphic properties of liquid crystals:



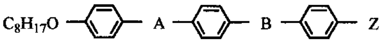
Compound	*A*	*B*	*Z*	Phase transitions/°C	Ref.
4-1	CH=N	—	NO_2	Cr 99 SmE (93) SmB 232 N 257 I	[92]
4-2	CH=N	—	CN	Cr 68 SmE 100 SmA 243 N 267 I	[93]
4-3	COO	COO	NO_2	Cr 114 SmA 210 N 224 I	[29, 88]
4-4	COO	COO	CN	Cr 116 N 229 I	[90]
4-5	OOC	OOC	NO_2	Cr 110 SmC$_{\mathrm{mod}}$ (108) SmA$_1$ 132 N 228 I	[94]
4-6	OOC	OOC	CN	Cr 129 SmA$_d$ 199 N 241 I	[91]
4-7	OOC	COO	NO_2	Cr 153 SmA 190 N 220 I	[88]
4-8	OOC	COO	CN	Cr 148 SmA 158 N 233 I	[95]
4-9	N=CH	COO	NO_2	Cr 115 N$_{\mathrm{re}}$ 132 SmA 196 N 243 I	[96]
4-10	N=CH	COO	CN	Cr 133 N 255 I	[96]
4-11	COO	CH=N	NO_2	Cr 131 SmA 245 N 251 I	[97]
4-12	COO	CH=N	CN	Cr 108 N$_{\mathrm{re}}$ 152 SmA 198 N 255 I	[98]
4-13	N=CH	OOC	NO_2	Cr 121 SmA 196 N 252 I	[99]
4-14	N=CH	OOC	CN	Cr 122 SmC$_{\mathrm{mod}}$ (119) SmA 172 N 262 I	[99]

Table 5. Mesomorphic properties of liquid crystals:



Compound	*A*	*B*	*Z*	Phase transitions/°C	Ref.
5-1	CH=N	OOC	NO_2	Cr 123 SmA 240 N 254 I	[96]
5-2	CH=N	OOC	CN	Cr 119 SmA$_1$ 147 N 266 I	[96]
5-3	COO	N=CH	NO_2	Cr 103 SmA 254 N 261 I	[96]
5-4	COO	N=CH	CN	Cr 98 SmA 119 N$_{\mathrm{re}}$ 166 SmA 204 N 264 I	[96]
5-5	CH=N	COO	NO_2	Cr 117 SmA 241 N 246 I	[96]
5-6	CH=N	COO	CN	Cr 113 N$_{\mathrm{re}}$ 138 SmA$_d$ 208 N 254 I	[96]
5-7	OOC	N=CH	NO_2	Cr 138 SmA$_1$ (128) N 253 I	[96]
5-8	OOC	N=CH	CN	Cr 113 SmA$_{\mathrm{mod}}$ 132 SmA 149 N 266 I	[96]
5-9	OOC	CH=N	NO_2	Cr 87 N$_{\mathrm{re}}$ (64) SmC (67) SmA 186 N 241 I	[96]
5-10	OOC	CH=N	CN	Cr 102 SmC$_2$ (99) SmC$_{\mathrm{mod}}$ 198 SmC 109 SmA 206 N 258 I	[96]
5-11	N=CH	OCH_2	NO_2	Cr 86 SmH 109 SmC 120.5 N 183 I	[91]
5-12	N=CH	OCH_2	CN	Cr 112 SmB 123 SmA 138 N 191 I	[104]
5-13	COO	CH=CH	NO_2	Cr 100 SmA 271 N 281 I	[90]
5-14	COO	CH=CH	CN	Cr 95.5 SmA (94.1) N$_{\mathrm{re}}$ 137.8 SmA 248.5 N 282.8 I	[90]
5-15	OOC	OCH_2	NO_2	Cr 117 N 161 I	[91]
5-16	OOC	OCH_2	CN	Cr 114.5 SmC$_{\mathrm{mod}}$ (110.5) SmA$_1$ 122 N 167 I	[91]

may affect the efficiency of the terminal NO_2 groups (compounds **3-2**, **3-11**, **3-13**, **3-15**, **4-3**, **4-5**, **4-7**, **4-9**, **4-11**, **4-13**, tables 3, 4 and [29, 30, 88, 90, 91, 97, 100–103]):



(III) *System (III)*

(a) A = COO, B = OOC
$T_{\mathrm{cl}} \rightarrow Z$: $H < F < CH_3 < OCF_3 < CF_3 < Cl \approx Br < OCH_3 < NO_2 < CN$
$T_{\mathrm{m}} \rightarrow Z$: $CH_3 < H < F < OCH_3 < CN < OCF_3 < NO_2 < Cl < Br < CF_3$

(b) A = COO, B = COO
$T_{\mathrm{cl}} \rightarrow Z$: $H < F < CH_3 < CF_3 < Br < OCF_3 < NO_2 < OCH_3 < CN$
$T_{\mathrm{m}} \rightarrow Z$: $OCH_3 < CH_3 < NO_2 < CN < H < F < OCF_3 < Cl < Br \approx CF_3$

(c) A = OOC, B = OOC
$T_{\mathrm{cl}} \rightarrow Z$: $H < F < CH_3 < OCF_3 < CF_3 < Cl \approx OCH_3 < Br < NO_2 < CN$
$T_{\mathrm{m}} \rightarrow Z$: $OCH_3 < OCF_3 < NO_2 < CH_3 < F < H < Cl < Br \approx CF_3 < CN$

(d) A = OOC, B = COO
$T_{\mathrm{cl}} \rightarrow Z$: $H < CH_3 < F < OCH_3 < NO_2 < Cl < OCF_3 < Br < CN$
$T_{\mathrm{m}} \rightarrow Z$: $CH_3 < CN < NO_2 < H < OCH_3 < F < OCF_3 < Cl < Br$

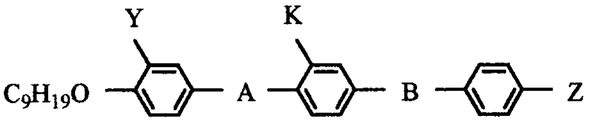
(e) A = COO, B = CH = N
$T_{\mathrm{cl}} \rightarrow Z$: $H < F < CH_3 < Cl < Br < OCH_3 < NO_2 < CN$
$T_{\mathrm{m}} \rightarrow Z$: $F < OCH_3 < Br < H < CN < CH_3 < Cl < NO_2$

(f) A = single bond, B = COO
$T_{\mathrm{cl}} \rightarrow Z$: $H < CH_3 < F < NO_2 < CF_3 < OCH_3 < Cl < CN < Br$
$T_{\mathrm{m}} \rightarrow Z$: $NO_2 < CN < CH_3 < F < OCH_3 < Cl < Br < CF_3$

(g) A = single bond, B = OOC
$T_{\mathrm{cl}} \rightarrow Z$: $H < F < CH_3 < Cl < Br < OCF_3 \approx CF_3 < OCH_3 < NO_2 < CN$
$T_{\mathrm{m}} \rightarrow Z$: $OCF_3 < OCH_3 < NO_2 < H < CN < CH_3 < F \approx CF_3 < Cl < Br$

It is important to note that decreasing the length of the alkoxy group from the octyloxy to the methoxy group

Table 6. Mesomorphic properties of liquid crystals:



Compound	*A*	*B*	*Y*	*K*	*Z*	Phase transitions/°C	d^a/Å	d^a/L	Ref.
6-1	COO	OOC	H	H	NO_2	Cr 164 SmA 242 N 243 I			[89]
6-2	COO	OOC	H	H	CN	Cr 140.5 SmA 227 N 249 I			[89]
6-3	OOC	COO	H	H	NO_2	Cr 156 SmA 198 N 219 I			[95]
6-4	OOC	COO	H	H	CN	Cr 143 SmA 202 N 226 I			[95]
6-5	OOC	OOC	H	H	NO_2	Cr 109 SmC_2 (96) SmC_{mod} 118 SmA_1 124 N_{re} 127 SmA_{dre} 138 N_{re} 156 SmA_d 195 N 224 I			[105]
6-6	OOC	OOC	H	H	CN	Cr 132 SmC (111) SmA_d 213 N 232 I			[91]
6-7	COO	COO	H	H	NO_2	Cr 116 SmA 218 N 222 I			[106]
6-8	COO	COO	H	H	CN	Cr 121 N_{re} (116) SmA_d 198 N 229 I	40.87	1.31	[107]
6-9	COO	COO	NO_2	H	CN	Cr 111 SmA_d 136 N 157 I	40.12	1.29	[107]
6-10	COO	COO	Br	H	CN	Cr 96 SmA (83) SmA_d 155 N 181 I	42.04	1.35	[107]
6-11	COO	COO	Cl	H	CN	Cr 115 SmA (85) SmA_d 167 N 186 I	40.49	1.30	[107]
6-12	COO	COO	OCH_3	H	CN	Cr 117 SmA_d 151 N 159 I	40.12	1.29	[107]
6-13	COO	COO	H	NO_2	CN	Cr 76 SmC_2 (56) N 156 I			[108]
6-14	COO	COO	H	Br	CN	Cr 95 N 164 I			[108]
6-15	COO	COO	H	OCH_3	CN	Cr 116 N 153 I			[108]

[a] $T_{meas} = T_{N\text{-}I} - 40°C$.

Table 7. Mesomorphic properties of liquid crystals:

Compound	*Y*	*Z*	Phase transitions/°C	Ref.
7-1	H	NO_2	Cr 231 N (209) I	[109]
7-2	O_2N	NO_2	Cr 262 N 281 I	[110]
7-3	Cl	NO_2	Cr 202 N 270 I	[109]
7-4	Cl	Cl	Cr 226 N 246 I	[111]
7-5	NC	CN	Cr 331.5 N 353.5 I	[110]
7-6	Br	Br	Cr 255 Sm (125.5) N (252) I	[110]
7-7	F	F	Cr 210 I	[111]
7-8	CF_3	CF_3	Cr 174 Sm 221 I	[112]
7-9	CF_3O	OCF_3	Cr 135 Sm 162 N 193 I	[112]
7-10	CH_3	CH_3	Cr 231.5 N 236 I	[110]
7-11	CH_3O	OCH_3	Cr 222 N 300 I	[110]
7-12	H_2N	NH_2	Cr 323 N > 350 decomp.	[109]

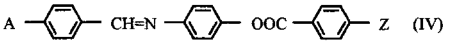
in system (IIIa) changes the efficiency of the terminal substituents [109, 113]:

$$T_{cl} \rightarrow Z\text{: } H < CF_3 < F < CH_3 < Br < Cl < OCH_3 \approx NO_2 < CN$$

$$T_m \rightarrow Z\text{: } F < H < CN < Cl < NO_2 < CH_3 < Br < OCH_3 < CF_3.$$

The odd–even effect in the clearing points can be responsible for these changes, since the last series has an odd alkoxy chain and the system (IIIa) has an even alkoxy chain.

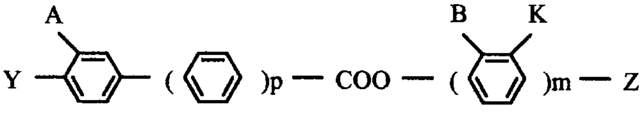
Similar results have been found for other liquid crystalline derivatives represented by the system (IV), where the efficiency of the terminal group *Z* (ΔT_N is the nematic range) is very sensitive to the structure of another terminal substituent *A* [114]:



System (IV)

$$\begin{aligned} A = CH_3 \quad & T_{cl} \rightarrow Z\text{: } CF_3 < F < CH_3 < Br < Cl < OCH_3 < NO_2 \\ & T_m \rightarrow Z\text{: } F < OCH_3 < Cl < NO_2 < Br < CH_3 < CF_3 \\ & \Delta T_N \rightarrow Z\text{: } CF_3 < CH_3 < Br < F < Cl < NO_2 < OCH_3 \\ A = CF_3 \quad & T_{cl} \rightarrow Z\text{: } CF_3 < F < NO_2 < Cl \approx Br < CH_3 < OCH_3 \\ & T_m \rightarrow Z\text{: } F < OCH_3 < Cl < Br < CH_3 < NO_2 \approx CF_3 \\ & \Delta T_N \rightarrow Z\text{: } CF_3 < NO_2 \approx CH_3 < F < Br < Cl < OCH_3 \\ A = NO_2 \quad & T_{cl} \rightarrow Z\text{: } CF_3 < F < NO_2 < Cl < CH_3 < Br < OCH_3 \\ & T_m \rightarrow Z\text{: } CH_3 < F < OCH_3 < CF_3 < Cl < Br < NO_2 \\ & \Delta T_N \rightarrow Z\text{: } CF_3 < NO_2 < F < Br < Cl < CH_3 < OCH_3. \end{aligned}$$

Table 8. Physico-chemical properties of liquid crystals:

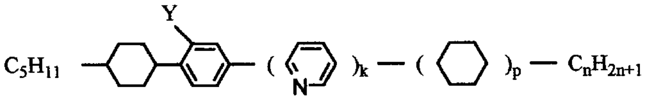


Compound	Y	A	p	B	K	m	Z	Phase transitions/°C	$\Delta\varepsilon$[a]	Ref.
8-1	$C_6H_{13}O$	H	0	H	H	1	OC_4H_9	Cr 63 N 88.5 I		[214]
8-2	$C_6H_{13}O$	NO_2	0	H	H	1	OC_4H_9	Cr 51.4 Sm 62.3 I	−7.9	[215]
8-3	$C_6H_{13}O$	H	0	NO_2	H	1	OC_4H_9	Cr 40 I	−5.7[b]	[216]
8-4	$C_6H_{13}O$	NO_2	0	NO_2	NO_2	1	OC_4H_9	Cr 141 I	−16.5	[215]
8-5	$C_6H_{13}O$	CN	0	NO_2	NO_2	1	OC_4H_9	Cr 164 I	−19.5	[215]
8-6	C_7H_{15}	H	0	H	H	1	OC_4H_9	Cr 46 N 57 I		[67]
8-7	C_7H_{15}	H	0	NO_2	H	1	OC_4H_9	Cr 56 I	−5.5[b]	[216]
8-8	C_7H_{15}	H	0	NO_2	NO_2	1	OC_4H_9	Cr 58 I	−18.0	[215]
8-9	$C_8H_{17}O$	H	1	H	H	0	C_3H_7	Cr 82.5 Sm 103 I		[217]
8-10	$C_8H_{17}O$	NO_2	1	H	H	0	C_3H_7	Cr 57 Sm (47) I		[218]
8-11	$C_8H_{17}O$	Cl	1	H	H	0	C_3H_7	Cr 51 I		[218]
8-12	$C_8H_{17}O$	F	1	H	H	0	C_3H_7	Cr 46 Sm 59.5 I		[219]
8-13	C_5H_{11}	H	1	H	H	1	OC_4H_9	Cr 116 Sm 154 N 205 I		[220]
8-14	C_5H_{11}	H	1	NO_2	NO_2	1	OC_4H_9	Cr 103 N 134 I	−20.0	[215]
8-15	C_5H_{11}	H	1	CN	CN	1	OC_4H_9	Cr 150.8 N 153.6 I		[221]

[a] Extrapolated from the liquid crystalline mixture at 20°C.

[b] Extrapolated from the liquid crystalline mixture at 21°C.

Table 9. Mesomorphic properties of liquid crystals:

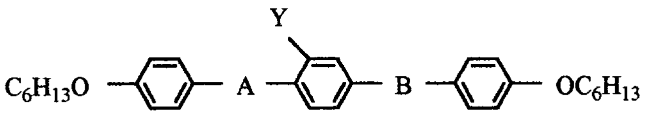


Compound	k	p	n	Y	Phase transitions/°C	Ref.
9-1	1	0	2	H	Cr 65.8 Sm 78 N 168 I	[65]
9-2	1	0	2	NO_2	Cr 61 I	[65]
9-3	1	0	2	NH_2	Sm 80 N 128 I	[65]
9-4	1	0	2	F	Cr 60 N 142 I	[65]
9-5	1	1	2	H	Cr 50 Sm 200 N 299 I	[65]
9-6	1	1	2	NO_2	Cr 87 N 168 I	[65]
9-7	1	1	2	NH_2	Cr 98.1 Sm 135 N 212.4 I	[65]
9-8	1	1	2	F	Cr 104.6 N 270 I	[65]
9-9	0	1	5	H	Cr 50 Sm 196 I	[222]
9-10	0	1	5	NO_2	Cr 51.2 N 57 I	[32]
9-11	0	1	5	CN	Cr 62.8 Sm (43.1) N 79.5 I	[32]
9-12	0	1	5	F	Cr 61 Sm 79.2 N 142.8 I	[32]
9-13	0	1	5	Cl	Cr 46.1 N 96.1 I	[32]
9-14	0	1	5	Br	Cr 40.5 N 80.8 I	[32]
9-15	0	1	5	CH_3	Cr 55.5 N 86.5 I	[32]
9-16	0	1	5	NH_2	Cr 67 Sm 163 I	[32]

Changing the molecular core and the second terminal substituent *A* may affect these orders again [115–117]. These results reveal the importance of the effect of molecular structure of terminally nitro substituted liquid crystals on their mesomorphic properties.

It is very interesting to compare the mesomorphic properties of the nitro substituted derivatives with those of the corresponding cyano derivatives which are still the most important components of liquid crystal materials for the twisted- and super-twisted nematic liquid crystal displays (STN-LCDs) [6, 7, 65, 66, 70, 118–122]. It follows from the above results, and the phase transition temperatures of compounds **1-1** and **1-2**; **1-7** and **1-8**; **1-11**–**1-16**; **2-1**–**2-10**; **3-2** and **3-3**; **3-11**–**3-16**; **4-1**–**4-14**; **5-1**–**5-16**; **6-1**–**6-8** (tables 1–6 and references [28, 30, 67, 70, 76–78, 82, 88–93, 95–97, 99, 105–107, 115, 116, 123–161]) that nitro substitution produces liquid crystals which exhibit lower clearing points than those of the corresponding cyano derivatives. The opposite situation has been observed in some other liquid crystalline derivatives

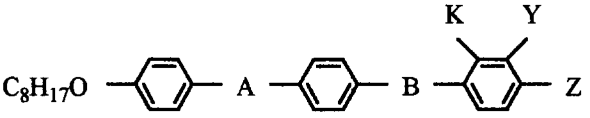
Table 10. Physico-chemical properties of liquid crystals:



Compound	*A*	*B*	*Y*	Phase transitions/°C	$\Delta\varepsilon^a$	Ref.
10-1	COO	OOC	H	Cr 121 N 211.5 I	-0.85	[223]
10-2	COO	OOC	NO_2	Cr 89 N 154 I	-1.90	[223]
10-3	COO	OOC	CN	Cr 85 N 164 I		[223]
10-4	COO	OOC	Cl	Cr 82.5 N 179 I	-0.90	[223]
10-5	COO	OOC	Br	Cr 97 N 163 I		[224]
10-6	COO	OOC	CH_3	Cr 87.8 N 171.8 I		[225]
10-7	OOC	OOC	H	Cr 93 N 206 I		[226]
10-8	OOC	OOC	NO_2	Cr 89 N 165 I	-3.30^b	[227]
10-9	OOC	OOC	CN	Cr 85 N 165 I	-3.35^c	[227]

[a] $T_{meas} = T_{N\text{-}I} - 25$°C.
[b] $T_{meas} = T_{N\text{-}I} - 75$°C.
[c] $T_{meas} = T_{N\text{-}I} - 60$°C.

Table 11. Mesomorphic properties of liquid crystals:



Compound	*A*	*B*	*K*	*Y*	*Z*	Phase transitions/°C	Ref.
11-1	COO	COO	H	H	H	Cr 118 SmA 129 N 140 I	[87]
11-2	COO	COO	H	NO_2	H	Cr 119 SmA (106) N 120 I	[106]
11-3	COO	COO	NO_2	H	H	Cr 120 N (110) I	[106]
11-4	COO	OOC	H	NO_2	H	Cr 113 SmA_1 (82) N 134 I	[228]
11-5	COO	OOC	NO_2	H	H	Cr 95 N 95 I	[106]
11-6	OOC	OOC	H	H	H	Cr 118 N 135 I	[87]
11-7	OOC	OOC	H	NO_2	H	Cr 106 SmA_2 (112) N 131 I	[228]
11-8	OOC	OOC	NO_2	H	H	Cr 94 N 98 I	[106]
11-9	OOC	COO	H	H	H	Cr 153 N (138) I	[87]
11-10	OOC	COO	H	NO_2	H	Cr 119 SmA (109) N 123 I	[106]
11-11	OOC	COO	NO_2	H	H	Cr 107 N (101) I	[106]
11-12	COO	OOC	H	NO_2	NO_2	Cr 101 SmA_1 156 I	[228]
11-13	COO	OOC	H	NO_2	F	Cr 112 SmA_1 142 I	[228]
11-14	COO	OOC	H	NO_2	Cl	Cr 130 SmA_1 155 I	[228]
11-15	COO	OOC	H	NO_2	CH_3	Cr 133 Sm (77) SmA_1 (90) N 147 I	[228]
11-16	COO	OOC	H	NO_2	OCH_3	Cr 118 N 171 I	[228]

(compounds **1-9** and **1-10**, table 1 and [67, 162–164]). It has been shown that for some liquid crystalline compounds, increasing the length of the alkoxy/alkyl groups usually decreases the difference in the clearing temperatures between the corresponding nitro and cyano derivatives [67, 76, 79, 80, 89–91, 94, 96, 129, 133, 135, 139, 140, 147, 159, 165], and in some cases it can lead to a higher stability of the mesophases for the former compounds compared with the latter derivatives [67, 89, 90, 96]. This can also be achieved by changing the alkoxy group length [130] or the orientation of the linking groups [141].

The nematic ranges can be wider either for the nitro derivatives (see, for example compounds **4-1** and **4-2**; **4-5** and **4-6**; **5-9** and **5-10**; **5-11** and **5-12**; **6-5** and **6-6**; tables 4–6) or for the cyano derivatives (compounds **2-1**–**2-6**; **2-9** and **2-10**; **3-2** and **3-3**; **4-3** and **4-4**; **4-7**–**4-14**; **5-1**–**5-8**; **5-13**–**5-16**; **6-1**–**6-4**; **6-7** and **6-8**; tables 2–6).

The melting temperatures can be higher for the nitro derivatives (see for example, compounds **1-7**–**1-12**; **1-15** and **1-16**; **2-7** and **2-8**; **3-2** and **3-3**; **4-1** and **4-2**; **4-7** and **4-8**; **4-11** and **4-12**; **5-1**–**5-8**; **5-13**–**5-16**; **6-1**–**6-4**; tables 1–6) or for the cyano derivatives (compounds **1-1** and **1-2**; **1-13** and **1-14**; **2-1**–**2-6**; **2-9** and **2-10**; **3-11**–**3-16**; **4-3**–**4-6**; **4-9** and **4-10**; **4-13** and **4-14**; **5-9**–**5-12**; **6-5**–**6-8**; tables 1, 2, 4–6) in comparison with those of the corresponding cyano and nitro derivatives, respectively. The opposite situations can be obtained by changing the molecular fragments (compounds **1-7**–**1-16**, table 1) or changing the linking groups (compounds **2-1**–**2-10**; **3-2**, **3-3**, **3-11**–**3-16**, **4-1**–**4-14**, **5-1**–**5-16**; **6-1**–**6-8**; tables 2–6) or by changing the length of the alkoxy/alkyl group [70, 89, 91–93, 96, 99, 137, 159] or replacing the alkoxy group by the corresponding alkyl group [89]. Higher melting temperatures and lower values of the anisotropy of polarizability of the nitro derivatives in comparison with those of the corresponding cyano derivatives, as well as a majority of the data on the melting temperatures discussed above, would not support the suggestion that increasing the anisotropy of polarizability leads to the increase of the melting points of liquid crystals [28, 110].

As is evident from tables 3–5, the difference in the nematic thermostabilities (ΔT) of the nitro and the corresponding cyano substituted octyloxy derivatives depends on the structure of their linking groups A, B in the following way, where SB is a single carbon–carbon bond:

$$\begin{aligned}\Delta T \rightarrow A, B\text{: } & \mathrm{COO, CH{=}CH < COO, N{=}CH < COO,} \\ & \mathrm{CH{=}N < COO, COO < OOC, OCH_2 < CH{=}N,} \\ & \mathrm{COO \approx N{=}CH, OCH_2 < COO, OOC \approx SB,} \\ & \mathrm{OCH_2 < CH{=}N, SB \approx N{=}CH, OOC < N{=}CH,} \\ & \mathrm{COO \approx CH{=}N, OOC < OOC, OOC \approx OOC,} \\ & \mathrm{COO \approx OOC, N{=}CH < SB, COO < SB,} \\ & \mathrm{OOC < OOC, CH{=}N.}\end{aligned}$$

Interestingly, the large difference in the nematic–isotropic phase transition temperatures between those of the nitro and the corresponding cyano derivatives can be achieved for three-ring compounds having only one linkage B—the ester group. The incorporation of the ester group COO as a linkage A into the molecular structure of three-ring octyloxy substituted derivatives gives less pronounced difference in the clearing points. Changing the orientation of this group results in the opposite situation. In other words, the replacement of the terminal nitro group by the cyano group in these compounds affects the efficiency of their linking groups.

The data collated in tables 3–5 reveal that the terminal nitro substitution of three-ring octyloxy derivatives containing OOC and $\mathrm{OCH_2}$ linking groups promotes the formation of the nematic as the only mesophase (compound **5-15**); for the cyano derivatives it can be achieved for compounds having one COO linkage B or COO, COO; N=CH, COO linking groups A, B (compounds **3-12**, **4-4**, **4-10**). The reentrant nematic phase is favoured for nitro derivatives having one $\mathrm{OCH_2}$ linkage B or N=CH, COO; OOC, CH=N linking groups A, B (compounds **3-15**, **4-9**, **5-9**). The stability of the reentrant nematic phase T_{Nre} in nitro derivatives is consistent with the following order of the linking groups A, B:

$$T_{\mathrm{Nre}} \rightarrow A, B\text{: } \mathrm{OOC, CH{=}N < SB, OCH_2 < N{=}CH, COO.}$$

For cyano derivatives this order is as follows (compounds **4-12**, **5-4**, **5-6**, **5-14**, tables 4, 5):

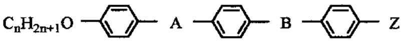
$$\begin{aligned}T_{\mathrm{Nre}} \rightarrow A, B\text{: } & \mathrm{COO, CH{=}CH < CH{=}N, COO < COO,} \\ & \mathrm{CH{=}N < COO, N{=}CH}\end{aligned}$$

From these results we can point out that terminal nitro and cyano substitution of three-ring octyloxy derivatives containing ester and azomethine linking groups favours the formation of the reentrant nematic phases in different degrees depending on the structure of the polar substituent, and positions and orientations of these linkages in the molecular structure. We have not observed any combination of the two linking groups used in the liquid crystals presented in tables 4, 5 (one of them is the ester and the other azomethine) which leads to the formation of the reentrant nematic or modulated smectic $\mathrm{A_{mod}}$ or smectic $\mathrm{C_{mod}}$ in both corresponding nitro and cyano derivatives. The incorporation of two ester linking groups with any orientations into the molecular core of the nitro and cyano derivatives does not create the reentrant phases or modulated smectic $\mathrm{A_{mod}}$ phase (tables 3, 4). The only mesophase, which always exists in both corresponding nitro and cyano substituted octyloxy derivatives shown in tables 3–5, is the nematic phase. However, its transition temperatures strongly depend on the molecular structure as discussed above.

Basically, the given molecular structures of the nitro and the corresponding cyano substituted octyloxy derivatives presented in tables 3–5, do not show the same phase sequences (cases of compounds **3-2** and **3-3**; **4-7** and **4-8**; **5-1** and **5-2** are open questions, since their smectic A phases have not yet been identified).

As can be seen from tables 4, 6, an increase in the alkoxy group length from the octyloxy (compound **4-5**) to the nonyloxy group results in the appearance of some additional phases: two reentrant nematic and one reentrant smectic $\mathrm{A_d}$, monotropic smectic $\mathrm{C_2}$ and the smectic $\mathrm{A_d}$ phases in compound **6-5**. For the corresponding cyano derivatives this effect is less pronounced—only one additional monotropic smectic C phase has appeared (compounds **4-6** and **6-6**). Similar results have been shown for other nitro and corresponding cyano derivatives having two ester linking groups (compounds **3-2** and **6-1**; **3-3** and **6-2**; **4-3** and **6-7**; **4-4** and **6-8**; **4-7** and **6-3**; **4-8** and **6-4**; tables 3, 4, 6).

In considering the mesomorphic properties of the homologous series which include compounds **3-2**, **3-3**, **3-11**–**3-16**, **4-1**–**4-14**, **5-1**–**5-16**, **6-1**–**6-8** (tables 3–6) it is useful to present the phase sequences between the crystalline and isotropic states of all these compounds in system (V):



(V) *System (V)*

(a) *A*=CH=N, *B*=single bond [92, 93]

Z=NO$_2$	*n*=1–3	phase N
	n=4	SmB, N
	n=5–9	SmE, SmB, N
Z=CN	*n*=5	SmE, SmB
	n=6	SmB, N
	n=7	SmE, SmB, N$_{re}$, SmA, N
	n=8, 9	SmE, SmA, N

(b) *A*=single bond, *B*=OCH$_2$ [91]

Z=NO$_2$	*n*=4	N
	n=5	SmH, SmG, SmA, N
	n=6, 7	SmH, SmG, N
	n=8, 9	SmG, N$_{re}$, SmA, N
	n=10	SmA, N
	n=11, 12	SmH, SmA
Z=CN	*n*=4	SmA, N
	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

(c) *A*=COO, *B*=CH=CH [90]

Z=NO$_2$	*n*=3, 4	N
	n=5–9	SmA, N
	n=10–12	SmA
Z=CN	*n*=4–7	SmA, N
	n=8, 9	SmA, N$_{re}$, SmA, N
	n=10	N$_{re}$, SmA, N
	n=12	SmA

(d) *A*=OOC, *B*=OCH$_2$ [91]

Z=NO$_2$	*n*=1–11	N
	n=12	N$_{re}$, SmA, N
	n=13	N$_{re}$, SmA
	n=14	SmA
Z=CN	*n*=5–7	SmA$_1$, N
	n=8	SmC$_{mod}$, SmA$_1$, N
	n=9	SmA$_2$, SmC$_{mod}$, SmA$_1$, N
	n=10	SmA$_2$, SmC$_{mod}$, SmA$_d$, N
	n=11	SmA$_2$, SmA$_d$, N
	n=12	SmA$_d$

(e) *A*=OOC, *B*=OOC [91, 94, 105, 106]

Z=NO$_2$	*n*=4	N
	n=5, 6	SmA, N
	n=7	SmA$_1$, N
	n=8	SmC$_{mod}$, SmA$_1$, N
	n=9	SmC$_2$, SmC$_{mod}$, SmA$_1$, N$_{re}$, SmA$_{dre}$, N$_{re}$, SmA$_d$, N
	n=10	SmC$_2$, SmC$_{mod}$, SmA$_d$, N
Z=CN	*n*=6	SmA$_2$, N
	n=7	SmA$_2$, SmA$_d$, N
	n=8	SmA$_d$, N
	n=9	SmC, SmA$_d$, N

(f) *A*=COO, *B*=COO [90, 106, 107, 156, 157]

Z=NO$_2$	*n*=5	N
	n=6	SmA$_d$, N
	n=7, 8	SmA, N
	n=9	SmA, N
Z=CN	*n*=6	SmB, N
	n=8	N
	n=9	N$_{re}$, SmA, N

(g) *A*=COO, *B*=OOC [88, 89, 106]

Z=NO$_2$	*n*=1–3	N
	n=4–9	SmA, N
	n=10–12	SmA
Z=CN	*n*=1–4	N
	n=5–11	SmA, N
	n=12	SmA

(h) *A*=OOC, *B*=COO [95, 106]

Z=NO$_2$	*n*=7	N
	n=8, 9	SmA, N
Z=CN	*n*=7	N
	n=8, 9	SmA, N

(i) *A*=COO, *B*=CH=N [97, 98]

Z=NO$_2$	*n*=5–8	SmA, N
Z=CN	*n*=5–7	SmA, N
	n=8	N$_{re}$, SmA, N

(j) *A*=CH=N, *B*=COO [96]

Z=NO$_2$	*n*=7	SmA$_d$, N
	n=8	SmA, N
	n=9, 10	SmA
Z=CN	*n*=7	N
	n=8	N$_{re}$, SmA$_d$, N
	n=9	*N*$_{re}$, SmC, SmA, N
	n=10	SmA, N

(k) *A*=CH=N, *B*=OOC [94, 96]

Z=NO$_2$	*n*=7–9	SmA, N
	n=10	SmA
Z=CN	*n*=7, 8	SmA$_1$, N
	n=9	SmA$_1$, N$_{re}$, SmA, N
	n=10	SmC$_2$, SmC, SmA, N

(l) *A*=COO, *B*=N=CH [96]

Z=NO$_2$	*n*=7, 8	SmA, N
	n=9, 10	SmA
Z=CN	*n*=7	SmA, N
	n=8–10	SmA, N$_{re}$, SmA, N

(m) *A*=OOC, *B*=N=CH [96]

Z=NO$_2$	*n*=8	SmA$_1$, N
	n=9, 10	SmC$_1$, N
	n=11, 12	SmC$_1$, SmA$_d$, N
Z=CN	*n*=8	SmA$_{mod}$, SmA, N
	n=9	SmA$_2$, SmC$_{mod}$, SmA, N
	n=10	SmA$_2$, SmC$_{mod}$, SmA, N

(n) $A=$ OOC, $B=$ CH=N [96]
$Z=\mathrm{NO_2}$ $n=7$ N
$n=8$ $\mathrm{N_{re}}$, SmC, SmA, N
$n=9$ SmC, SmA, N
$n=10$ SmA, N
$Z=$ CN $n=7$ $\mathrm{SmC_{mod}}$, SmA, N
$n=8$ $\mathrm{SmC_2}$, $\mathrm{SmC_{mod}}$, SmC, SmA, N
$n=9$, 10 $\mathrm{SmC_2}$ SmA, N

(o) $A=$ N=CH, $B=$ OOC [96, 99]
$Z=\mathrm{NO_2}$ $n=4$–11 SmA, N
$n=12$, 14 SmA
$Z=$ CN $n=4$–7 SmA, N
$n=8$, 9 $\mathrm{SmC_{mod}}$, SmA, N
$n=10$, 11 $\mathrm{SmC_2}$, $\mathrm{SmC_{mod}}$, SmA, N
$n=12$ $\mathrm{SmC_2}$, SmA, N
$n=14$ $\mathrm{SmC_2}$, SmA

(p) $A=$ N=CH, $B=$ COO [96]
$Z=\mathrm{NO_2}$ $n=6$, 7 N
$n=8$ $\mathrm{N_{re}}$, SmA, N
$n=9$ $\mathrm{N_{re}}$, SmC, SmA, N
$n=10$ SmA, N
$Z=$ CN $n=7$, 8 N
$n=9$, 10 SmA, N

(q) $A=$ N=CH, $B=\mathrm{OCH_2}$ [91, 104]
$Z=\mathrm{NO_2}$ $n=1$–5 N
$n=6$–10 SmH, SmC, N
$n=11$ SmH, SmF, SmC, $\mathrm{N_{re}}$, SmA, N
$n=12$ SmF, SmC, $\mathrm{N_{re}}$, SmA
$n=13$, 14 SmF, SmC, SmA
$Z=$ CN $n=1$, 2 N
$n=3$–8 SmB, SmA, N
$n=9$ SmB, SmC, $\mathrm{SmC_{mod}}$, SmA, N
$n=10$, 11 SmB, SmC, SmA, N
$n=12$–14 SmC, SmA

These results show that the reentrant phases and modulated smectic $\mathrm{C_{mod}}$ phase have not been observed simultaneously in the nitro and corresponding cyano derivatives; no reentrant nematic or modulated smectic $\mathrm{C_{mod}}$ phases have been observed for the nitro derivatives below the octyloxy (heptyloxy for the cyano derivatives).

The appearance of reentrant nematic phases in the nitro derivatives depends on the length of the alkoxy group (n) and the structures of the linking groups (A, B). The dependence of this phase on groups A and B can be expressed in the following way:

$N_{re} \rightarrow n\ (A, B)$: 8 (SB, $\mathrm{OCH_2}$; OOC, CH=N; N=CH, COO)
<9 (OOC, OOC) <11 (N=CH, $\mathrm{OCH_2}$)
<12 (OOC, $\mathrm{OCH_2}$).

A similar dependence can be derived for the cyano derivatives:

$N_{re} \rightarrow n\ (A, B)$: 7 (CH=N, SB) <8 (COO, CH=CH; COO, CH=N; CH=N, COO; COO, N=CH)
<9 (COO, COO; CH=N, OOC).

These results illustrate that the reentrant nematic phase is more evident in the octyloxy substituted nitro and cyano derivatives. Generally, the first appearance of this phase is more evident in greater numbers of the nitro derivatives than of the cyano derivatives. Only one compound exhibits three reentrant phases, and only this compound shows the reentrant smectic $\mathrm{A_d}$ phase [compound **6-5**, table 6 and system (V)e, $Z=\mathrm{NO_2}$, $n=9$]. Nitro derivatives show the reentrant nematic phase in phase sequences which contain some of the following mesophases: SmH, SmF, SmG, SmC, $\mathrm{SmC_2}$, $\mathrm{SmC_{mod}}$, SmA, $\mathrm{SmA_1}$, $\mathrm{SmA_d}$, $\mathrm{SmA_{dre}}$, N; for cyano derivatives, the reentrant nematic phase accompanies some of these mesophases: SmE, SmB, SmA, $\mathrm{SmA_d}$, $\mathrm{SmA_1}$, N. It is important to note that phase sequences which include the reentrant nematic phase can be different for corresponding nitro and cyano derivatives. If the reentrant nematic or modulated smectic $\mathrm{C_{mod}}$ phases have already disappeared with the increasing length of the alkoxy group in the nitro or cyano derivatives, no further reentrant or modulated smectic $\mathrm{C_{mod}}$ phases are observed with a further increase in alkoxy group length in these series. The appearance of the reentrant nematic phase has been shown in one [system (V)e, n] or two [system (V)b, d, p, q] members of the homologous series of nitro derivatives. For cyano derivatives the reentrant nematic phase can be seen in one [system (V)a, f, k] or two [system (V)j] or three [system (V)c, i, l] [98] members of the homologous series.

The modulated smectic $\mathrm{C_{mod}}$ phase is more pronounced in cyano derivatives, with its first appearance in a series depending on A, B groups as follows:

$\mathrm{SmC_{mod}} \rightarrow n\ (A, B)$: 7 (OOC, CH=N)
<8 (OOC, $\mathrm{OCH_2}$; N=CH, OOC)
<9 (OOC, N=CH; N=CH, $\mathrm{OCH_2}$).

This mesophase exists in one [system (V)q], two [system (V)d, m, n], three [system (V)d] or four [system (V)o] members of homologous series of the cyano derivatives.

Similar conclusions can be derived for the modulated smectic $\mathrm{A_{mod}}$ phase which has only been observed in three-ring cyano substituted alkoxy derivatives [system (V)m]. Replacing the alkoxy group by the corresponding alkyl group in some three-ring nitro derivatives containing two ester linking groups, introduces the modulated smectic $\mathrm{A_{mod}}$ phase [94].

As discussed for octyloxy derivatives, identical phase sequences have not been observed (comparing compounds with the same alkoxy chains) for homologous series of corresponding nitro and cyano derivatives (except some members showing only nematic phases with different phase transition temperatures and some other cases which require the identification of the smectic A and C phases).

These results show that the mesomorphic properties of terminally nitro substituted three-ring derivatives depend on their molecular structure, including the length of the alkoxy groups, and the structure and orientation of the linking groups. The differences in mesophases and transition temperatures observed in the corresponding 4-substituted nitro and cyano derivatives can be attributed to the difference in the electronic and geometric structures of the nitro [14–21, 23–27, 166–172] and cyano groups [25, 173, 174], which through intramolecular [14–21, 27, 31, 175–194] and intermolecular [27, 178, 195–202] interactions affect molecular packing and, consequently, phase formation [203, 204].

Terminal nitro substitution of polar liquid crystals, depending on their structures and the structures of the second polar or strong polar substituent, may produce no mesophases [72] or result in the formation of high melting and thermostable nematic phases (compound **7-2**, table 7 and [123]). Basically, two-ring 4,4′-dinitro substituted 1,4-phenylene derivatives and 4,4′-dinitroterphenyl are not mesomorphic [72, 123, 205–211]. The introduction of ester (or ester based) linking groups into the molecular core of ter- and quater-phenyls may create nematic phases exhibiting high melting and clearing points (compound **7-2**, table 7 and [111, 210–213]. Interestingly, for 4,4′-disubstituted liquid crystals having the same terminal substituents, the efficiency of mesophase formation can be expressed by the following orders (compounds **7-2**, **7-4**–**7-12**, table 7):

$$\begin{aligned} T_{\mathrm{cl}} \rightarrow Y, Z&: \mathrm{F, F < CF_3O, OCF_3 < CF_3, CF_3 < CH_3,}\\ &\quad \mathrm{CH_3 < Cl, Cl < Br, Br < O_2N, NO_2 < CH_3O,}\\ &\quad \mathrm{OCH_3 < NC, CN < H_2N, NH_2}\\ T_{\mathrm{m}} \rightarrow Y, Z&: \mathrm{CF_3O, OCF_3 < CF_3, CF_3 < F, F < CH_3O,}\\ &\quad \mathrm{OCH_3 < Cl, Cl < CH_3, CH_3 < Br, Br < O_2N,}\\ &\quad \mathrm{NO_2 < H_2N, NH_2 < NC, CN}\\ \Delta T_{\mathrm{N}} \rightarrow Y, Z&: \mathrm{F, F; CF_3, CF_3; Br, Br < CH_3, CH_3 < O_2N,}\\ &\quad \mathrm{NO_2 < Cl, Cl < NC, CN < CF_3O,}\\ &\quad \mathrm{OCF_3 < CH_3O, OCH_3.} \end{aligned}$$

Replacement of the COO group by CH=N significantly changes these orders [114]:

$$\begin{aligned} T_{\mathrm{cl}} \rightarrow Y, Z&: \mathrm{CF_3, CF_3 < F, F < CH_3, CH_3 < Br,}\\ &\quad \mathrm{Br < Cl, Cl < O_2N, NO_2}\\ T_{\mathrm{m}} \rightarrow Y, Z&: \mathrm{F, F < Cl, Cl < CH_3, CH_3 < CF_3,}\\ &\quad \mathrm{CF_3 < Br, Br < O_2N, NO_2}\\ \Delta T_{\mathrm{N}} \rightarrow Y, Z&: \mathrm{CF_3, CF_3 < O_2N, NO_2 < F, F < CH_3,}\\ &\quad \mathrm{CH_3 < Br, Br < Cl, Cl.} \end{aligned}$$

This again shows the effect of the molecular structure of nitro substituted liquid crystals on their mesomorphic properties.

2.1.2. *Lateral nitro substitution*

The introduction of the nitro group as a lateral substituent into the molecular core of liquid crystals usually leads to a decrease of their clearing temperatures compared with those of the parent compounds (compounds **6-8** and **6-9**, **6-13**; **8-1** and **8-2**–**8-5**; **8-6** and **8-7**, **8-8**; **8-9** and **8-10**; **8-13** and **8-14**; **9-1** and **9-2**; **9-5** and **9-6**; **9-9** and **9-10**; **10-1** and **10-2**; **10-7** and **10-8**; **11-1** and **11-2**, **11-3**; **3-1** and **11-4**, **11-5**; **11-6** and **11-7**, **11-8**; **11-9** and **11-10**, **11-11**; **3-2** and **11-12**; tables 3, 6, 8–11). This has been explained in terms of reducing intermolecular interactions and broadening of the molecules [2, 3, 5, 9, 32]. However, lateral nitro substitution can introduce mesomophases of enhanced thermostability in one-ring perfluoroalkyl substituted benzene derivatives; this has been explained in terms of the predominant influence of the balance between fluorophobic and fluorophilic interactions around the perfluoroalkyl groups on the packing of these molecules [62, 229, 230]. The importance of the position of lateral nitro groups and their quantity in the molecular core and molecular fragment is shown in tables 3, 6, 8, 11 (compounds **6-8** and **6-9**, **6-13**; **8-1**–**8-5**; **8-6**–**8-8**; **8-13** and **8-14**; **11-1**–**11-3**; **3-1** and **11-4**, **11-5**; **11-6**–**11-8**; **11-9**–**11-11**). In particular, nitro substitution in the *ortho*-position to linkage *B* of the systems presented in tables 3, 11 produces liquid crystals which exhibit only nematic phases with the lowest thermostabilities, while the corresponding nitro substitution in the *meta*-position produces liquid crystals that exhibit nematic and smectic A phases with lower clearing points than those of the corresponding laterally unsubstituted derivatives which exhibit mainly nematic phases. Similar results have been found for the nitro substituted two-ring derivatives **8-2** and **8-3** (table 8) and for the three-ring derivatives **6-9** and **6-13** (table 6). Additionally, we see the disappearance of the smectic A phase and formation of the monotropic smectic C phase in compound **6-13**. These findings can be explained in terms of increased conjugation between the nitro (which is introduced in the *ortho*-position to the ester linkage) and ester linking groups which might increase molecular non-planarity and non-linearity.

Increasing the number of lateral nitro groups in the molecular core of a liquid crystal decreases the clearing temperature further, or leaves a non-mesomorphic behaviour unchanged (compounds **8-1** and **8-2**–**8-4**; **8-6** and **8-7**, **8-8**; table 8).

Lateral nitro substitution may increase melting temperatures (see for example, compounds **8-6** and **8-7**; **9-5** and **9-6**; **9-9** and **9-10**; **11-1** and **11-2**, **11-3**; tables 8, 9, 11) or decrease them (see for example, compounds **6-8** and **6-9**, **6-13**; **8-1** and **8-2**, **8-3**; **8-9** and **8-10**; **8-13** and **8-14**; **9-1** and **9-2**; **10-1** and **10-2**; **10-7** and **10-8**; **3-1** and **11-4**, **11-5**; **11-6** and **11-7**, **11-8**; **11-9** and **11-10**,

11-11; **3-2** and **11-12**; tables 3, 6, 8–11) in comparison with those of the corresponding parent compounds. Increasing the number of lateral NO_2 groups increases the melting temperatures (compounds **8-2**–**8-4**; **8-7**, **8-8**; table 8), while the position of the lateral nitro group in the molecular structure also influences the melting points (compounds **6-9** and **6-13**; **8-2** and **8-3**; **11-2** and **11-3**; **11-4** and **11-5**; **11-7** and **11-8**; **11-10** and **11-11**, tables 6, 8, 11). In particular, for compounds presented in table 11, nitro substitution in the *ortho*-position to the ester linkage can lead to a higher melting point (compounds **11-2** and **11-3**) or lower melting point (compounds **11-4** and **11-5**; **11-7** and **11-8**; **11-10** and **11-11**) compared with that of the corresponding derivatives having the nitro group in the *meta*-position in respect to the ester linkage.

The introduction of other lateral substituents into the corresponding liquid crystalline systems also reduces the clearing temperatures and affects melting points and nematic ranges in different degrees depending on the structures of the lateral substituents and of the liquid crystals as follows.

Compounds $T_{cl} \rightarrow Y$: $NO_2 < OCH_3 < Br < Cl < H$
6-8–**6-12**, $T_m \rightarrow Y$: $Br < NO_2 < Cl < OCH_3 < H$
table 6: $\Delta T_N \rightarrow Y$: $OCH_3 < Cl < NO_2 < Br < H$.

Compounds $T_{cl} \rightarrow K$: $OCH_3 < NO_2 < Br < H$
6-8, **6-13**–**6-15**, $T_m \rightarrow K$: $NO_2 < Br < OCH_3 < H$
table 6: $\Delta T_N \rightarrow K$: $H < OCH_3 < Br < NO_2$.

Compounds $T_{cl} \rightarrow A$: $Cl < NO_2 < F < H$
8-9–**8-12**, $T_m \rightarrow A$: $F < Cl < NO_2 < H$.
table 8:

Compounds $T_{cl} \rightarrow Y$: $NO_2 < NH_2 < F < H$
9-1–**9-4**, $T_m \rightarrow Y$: $F < NO_2 < H$
table 9: $\Delta T_N \rightarrow Y$: $NO_2 < NH_2 < F < H$.

Compounds $T_{cl} \rightarrow Y$: $NO_2 < NH_2 < F < H$
9-5–**9-8**, $T_m \rightarrow Y$: $H < NO_2 < NH_2 < F$
table 9: $\Delta T_N \rightarrow Y$: $NH_2 < NO_2 < H < F$.

Compounds $T_{cl} \rightarrow Y$: $NO_2 < CN < Br < CH_3 < Cl < F < NH_2 < H$
9-9–**9-16**, $T_m \rightarrow Y$: $Br < Cl < H < NO_2 < CH_3 < F < CN < NH_2$
table 9: $\Delta T_N \rightarrow Y$: NH_2, $H < NO_2 < CN < CH_3 < Br < Cl < F$.

Compounds $T_{cl} \rightarrow Y$: $NO_2 < Br < CN < CH_3 < Cl < H$
10-1–**10-6**, $T_m \rightarrow Y$: $Cl < CN < CH_3 < NO_2 < Br < H$
table 10: $\Delta T_N \rightarrow Y$: $NO_2 < Br < CN < CH_3 < H < Cl$.

Compounds $T_{cl} \rightarrow Y$: $NO_2 \approx CN < H$
10-7–**10-9**, $T_m \rightarrow Y$: $CN < NO_2 < H$
table 10: $\Delta T_N \rightarrow Y$: $NO_2 < CN < H$.

It has been proposed that an increase in the clearing points of liquid crystals may be correlated with the decreasing van der Waals volume of their lateral substituents [32]: $NO_2 < CN < Br < CH_3 < Cl < NH_2 < F < H$. However, some of the presented results (even the data in [32]) do not support this suggestion. As can be seen from table 8, the replacement of one of the nitro groups in compound **8-4** or two nitro groups in compound **8-14** by cyano groups enhances their melting temperatures but does not change the non-mesomorphic character (compound **8-5**), or increase the nematic thermostability (compound **8-15**).

It is evident from tables 3, 11 that lateral nitro substitution affects the efficiency of the linking groups *A*, *B* (compounds **11-1**–**11-3**; **3-1** and **11-4**, **11-5**; **11-6**–**11-8**; **11-9**–**11-11**) as follows.

Laterally unsubstituted compounds: OOC, OOC < OOC, COO < COO, COO < COO, OOC; compounds with the nitro group introduced in the *meta*-position to the linkage *B*: COO, COO < OOC, COO < OOC, OOC < COO, OOC; compounds with the nitro group introduced in the *ortho*-position to the linkage *B*: COO, OOC < OOC, OOC < OOC, COO < COO, COO.

The efficiency of the terminal substituents, compare with the system (IIIa) (compounds **11-12**–**11-16**) is in the order:

$$T_{cl} \rightarrow Z\text{: } H < F < CH_3 < Cl < NO_2 < OCH_3.$$

The results presented reveal that the effect of nitro substitution in achiral calamitic liquid crystals on their mesomorphic properties depends on their molecular structures and the quantity and positions of the nitro groups introduced there. Similar findings have been reported for other terminally [67, 135, 163, 231–246] and laterally [9, 163, 247–253] nitro substituted liquid crystalline derivatives. The formation of the smectic D phase in some laterally nitro substituted biphenyl acids has been studied in [254–268]. The mesomorphic properties of liquid crystals laterally substituted by nitro-containing molecular fragments have been discussed in [269–271].

The mesomorphic properties of terminally and laterally nitro substituted liquid crystals can be explained in terms of the predominant influence of their molecular packing [203, 204, 272]. Indeed, the electronic and geometric structure of the nitro group affects molecular packing [273] through intramolecular [14–21, 27, 31, 175–194] and intermolecular [27, 178, 195–202] interactions. Anisotropic dispersion interactions, and consequently the anisotropy of polarizability, also influence the packing and hence the stability of the mesophases, but play a secondary role compared with steric factors [204]. Other molecular aspects, such as association [198] or dipole–dipole attraction in polar liquid crystals, which can influence molecular packing, also affect the stability of the mesophases [204].

2.2. *X-ray data*

It has been shown that X-ray diffraction (XRD) of liquid crystals is a useful method for studying the effects of the association of molecules on the structure of mesophases and consequently on the properties of liquid crystals formed by these molecules [274–278]. The investigation of polar liquid crystals by XRD shows not only the existence of a layer structure in the smectic phase of these compounds, but also periodic density fluctuations in the nematic phase having a period d. The layers involve swarms containing tens to hundreds of molecules and are characterized by a correlation length ξ defined directly from the width of the diffraction peak. For the nematic phase of some two-ring cyano derivatives it has been shown that the ratio d/L, where L is a molecular length, is about 1.2–1.5 [274–276, 278]. 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 liquid crystals, and characterizes in particular the degree of overlap of the molecular cores on dimer formation. Further XRD investigations of the nematic phase of polar liquid crystals revealed in some cases the simultaneous existence of two fluctuating layer structures with incommensurate periods d_1 and d_2, where $d_1 < L$ and $L < d_2 < 2L$ [274, 275, 277, 278].

For two-ring nitro derivatives, only one density wave with a characteristic period d is observed (compounds **2-1**, **2-7**, **2-9** table 2 and [75, 81, 83, 92, 279–282]), with the ratio $d/L > 1$ recorded in their smectic A phases. Replacement of the terminal nitro group by the cyano group in liquid crystalline compounds results in increasing the ratio d/L (compounds **2-9** and **2-10**, table 2 and [83, 137, 154, 155, 165, 279, 282–288]). Thus the level of molecular overlapping in the formation of the dimers is higher for the nitro derivatives than for the corresponding cyano derivatives. It has been reported that the replacement of the nitro group by the cyano group in 4-*n*-alkylphenyl 3-methyl-4-(4-nitrobenzyloxy)benzoates results in a decrease in average rate of thermal expansion of the layers and a change of sign of the curvature of the thermal dependence of the layer spacing in the smectic A phase [237]. The different d/L values probably result from significantly different electron density distributions in the molecular structure (for pyridine derivatives this is shown in [289]) and steric factors which are responsible for the type of dimerization.

As can be seen from table 6, lateral substitution of the presented liquid crystal system not only changes its mesomorphic properties, but also the ratio d/L in the following order, giving its lowest value to the laterally nitro substituted derivative **6-9** (compounds **6-8**–**6-12**):

$$d/L \rightarrow Y\text{: } OCH_3 \approx NO_2 < Cl < H < Br.$$

Similar results have been reported for other terminally and laterally nitro substituted liquid crystalline derivatives [59, 60, 75, 81, 88, 90, 163, 196, 229, 270, 290–296].

3. Dielectric properties

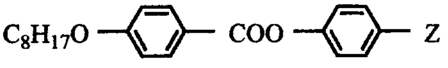
The relationship between the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are, respectively, the dielectric constants parallel and perpendicular to the nematic director **n**) and the molecular structure of liquid crystals is described by the theory of Maier and Meier [297]:

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

where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$; $\Delta\alpha = (\alpha_\parallel - \alpha_\perp)$ 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 liquid crystals with different nematic–isotropic phase transition temperatures $T_{N\text{-}I}$ can only be made at a constant reduced temperature $\tau = T_{meas}/T_{N\text{-}I}$ [120]. Tables 8, 10, 12 present data on the dielectric properties of liquid crystalline compounds

Table 12. Physico-chemical properties of liquid crystals:



Compound	Z	μ/D	$\varepsilon_\perp{}^a$	$\Delta\varepsilon^a$	$\Delta\varepsilon^a/\varepsilon_\perp{}^a$	$g(T_{N\text{-}I})$	$n_\perp{}^{a,b}$	$\Delta n^{a,b}$	$K_{11}{}^a \times 10^7$ /dyn	$K_{33}/K_{11}{}^a$	η /cSt	$\gamma_1{}^c$/ P	k_p	Ref.
2-1	NO_2	6.4	11.0	12.0	1.09	0.652	1.515	0.121	2.77	1.48	22.5^c	0.47	0.6072^e	[298-301]
2-2	CN	6.6	9.5	12.9	1.36	0.618	1.502	0.125			18.5^d		0.6010^f	[298, 302]

[a] $T_{meas} = T_{N\text{-}I} - 5°C$.
[b] $\lambda = 546$ nm.
[c] $T_{meas} = 63°C$.
[d] $T_{meas} = 71.5°C$.
[e] The value of the density is extrapolated to that at $T_{meas} = 93.8°C$.
[f] $T_{meas} = 93.8°C$.

measured at a constant reduced temperature and extrapolated from the liquid crystalline mixtures at 20–21°C. According to [120], 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 liquid crystals, and liquid crystals with a narrow nematic range.

The data on the dielectric properties of compounds presented in tables 10, 12 show that the introduction of a lateral nitro group or replacement of a terminal (lateral) nitro group by a cyano group increases the dielectric anisotropy (in absolute value) due to the dipole moment ($\mu NO_2 = 4.01$ D, $\mu CN = 4.05$ D [22]) and molecular polarizability [28] being increased (compounds **10-1** and **10-2**; **10-8** and **10-9**; **2-1** and **2-2**; and [303]). The opposite situation has been found for the corresponding lateral chloro substituted derivative **10-4**; this is due to the reduced dipole moment of the Cl group ($\mu = 1.59$ D) in comparison with that of the nitro group [22]. Interestingly, terminal nitro substitution of the two-ring derivative presented in table 12, results in a $\Delta\varepsilon/\varepsilon_\perp$ value is close to unity and hence is favourable for improving the electro-optical steepness of supertwisted nematic displays [304].

An increase in the number of lateral NO_2 groups introduced into the molecular structure of weakly polar liquid crystals enhances the absolute values of the negative dielectric anisotropy (compounds **8-2**–**8-4**, **8-7** and **8-8**; **8-14**; table 8). This result can be explained in terms of the pronounced transverse contribution of the individual dipole moments of the lateral nitro substituents to the overall molecular dipole moment relative to the director, see equation (1). Interestingly, replacement of a lateral nitro group by a cyano group (compounds **8-4** and **8-5**, table 8) further increases the negative dielectric anisotropy (in absolute value) due to the transverse component of the dipole moment being increased [22]. Similar effects on the dielectric properties of other liquid crystalline derivatives, having terminal or lateral nitro substituents, have been demonstrated in [116, 237, 305, 306] and [106, 215, 307], respectively.

It has been shown that mesogenic molecules possessing strongly polar terminal groups form associated pairs. Both head-to-head and head-to-tail pairing occurs [195, 197, 308, 309], but antiparallel association predominates and reduces the effective dipole moment [198]:

$$\mu_{\text{eff}}^2 = g\mu^2 \tag{2}$$

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

where $\varepsilon_i^\infty = 1.05n_i^2$ and g is the correlation factor characterizing the association tendency. For non-associating systems g is equal to 1. The data collated in table 12 show that all compounds under investigation exhibit the g values which are lower than 1, indicating an antiparallel association. Replacement of the terminal nitro group by cyano decreases factor g, i.e. enhances the association tendency (compounds **2-1** and **2-2**).

It is well known that the reorientation of molecules about their short and long axes can be characterized by the corresponding values of the activation energy derived from dielectric relaxation studies [310, 311]. This activation energy has been correlated with the character of molecular associations in the mesophases [312, 313]. Liquid crystalline nitro derivatives have been the subject of numerous dielectric relaxation experiments for many years [227, 284, 299, 303, 312, 314–316]. However, due to the differences in the values of the activation energy obtained for the same compounds [284, 312] and the little understood dielectric relaxation mechanism in the mesophases [310], it is difficult to analyse these data (which have been used with the results of Kerr effect experiments [144, 223, 298, 314, 317] for the study of molecular dynamics in nitro derivatives [318]).

4. Optical properties

The phenomenological relationship between refractive index and electric polarization is defined as [319, 320]:

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

where the mean polarizability $\alpha^* = (\alpha_\parallel + 2\alpha_\perp)/3$ and the mean refractive index is given by $n^{*2} = (n_e^2 + 2n_o^2)/3$ (n_o is the ordinary and n_e the extraordinary refractive index, respectively). From equation (4) and the previous section, it follows that nitro substituted compounds, which have smaller induced polarizability of their highly conjugated π-electron system [28], exhibit an optical anisotropy $\Delta n = n_e - n_o$ smaller than that of the corresponding cyano derivatives (compounds **2-1** and **2-2**, table 12 and [303, 314, 321]). These findings are supported by measurement of the anisotropy of polarizability ($\Delta\alpha/\text{Å}^3$) of the C_{Ar}–X bonds of mono-substituted benzenes; this increases, depending on the substituent X, as follows [28]: F $(0.5) <$ CH_3 $(1.2) <$ Cl $(2.5) <$ Br $(3.9) <$ NO_2 $(4.0) <$ CN (4.4).

5. Molecular packing

It has been shown that liquid crystal molecular packing plays a very important role in the creation of mesophases [272, 322] and defines their optical properties [319]. The molecular packing coefficient may be expressed as [323]:

$$k_p = N_A V\rho/M \tag{5}$$

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

As can be seen from table 12, replacement of the terminal nitro group by cyano in two-ring derivatives results in a decrease of the molecular packing coefficient (compounds **2-1** and **2-2**, table 12 and [74, 314]). A similar increase in density has been reported for a three-ring laterally nitro substituted derivative in comparison with that of the corresponding cyano derivative [227]. These results can be associated with the difference in the energy of intermolecular interactions—(and therefore with the difference in the activation energy of the rotational viscosity of these compounds [323].

6. Visco-elastic properties

It has been shown that nematic liquid crystalline materials for display applications should have a low viscosity in order to give acceptable response times to LCDs [120, 324]. From the results on the kinematic viscosity η and rotational viscosity γ_1 presented in table 12, the nitro substituted derivative **2-1** (see also [74, 325]) exhibits similar viscous behaviour to that of the corresponding cyano derivative **2-2**.

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 [326]. As can be seen from table 12 and from [119, 303], the nitro substituted derivative **2-1** exhibits a moderate value the ratio K_{33}/K_{11} compared with that of cyano substituted two-ring liquid crystalline derivatives ($K_{33}/K_{11} = 1.06 - 1.68$) [7].

7. Summary

The effects of terminal and lateral nitro substitution of achiral calamitic liquid crystals on their physico-chemical properties 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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