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Halogenation in achiral liquid crystals: terminal and linking substitutions

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Halogenation in achiral liquid crystals: terminal and linking substitutions

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The effect on the physico-chemical properties of achiral liquid crystals of introducing halogen atoms into their terminal and linking groups is discussed and rationalized in terms of existing theories; a comparison is made with the corresponding hydrogenated and other well-known groups.

1. Introduction

With the use of liquid crystal displays (LCDs) in information technology, the subject of liquid crystalline materials is particularly rich and diverse. Today's commercial applications of liquid crystalline materials based on halogenated compounds (especially fluorinated) clearly show the beneficial effects of halogenation, and the numerous ways in which LCD technology has taken practical advantage of these effects [1–6]. This review focuses on the characteristic substituent effects that underline the physico-chemical properties of achiral liquid crystals containing halogenated terminal and linking groups, particularly those important to the design of commercial liquid crystalline materials for display applications. When possible, the physico-chemical properties of achiral LCs having halogenated substituents will be compared with those of the corresponding compounds with hydrogenated and other well-known groups.

Many of the characteristic effects of halogenation can be anticipated by comparing some fundamental atomic properties of the halogens with those of hydrogen (table 1). Among the halogens, fluorine exhibits the highest ionization potential and lowest polarizability leading to weak intermolecular interactions [15, 16], low surface energies, and low refractive indexes for perfluorocarbons [7]. Due to the high electronegativity of fluorine, C–F bonds, having high ionic character, are the most polar of carbon–halogen among bonds. Halogen atoms linked to an unsaturated carbon atom or an aromatic ring exhibit an electron-accepting inductive effect and an electron-donating conjugation effect, decreasing in the sequence: F > Cl > Br > I. Among the halogens, the fluorine atom has the smallest covalent radius, close to that of the carbon atom, resulting in conditions for maximum overlapping of the p orbitals. Therefore, despite its highest electronegativity, the fluorine atom shows the most pronounced electron-donating conjugation effect among all the halogens [7, 8, 17–20].

In the last decades, the design and synthesis of liquid crystals containing fluoro-substituted terminal, linking and lateral groups have attracted much interest owing to their remarkable physico-chemical properties which make them very useful for display applications [1–5, 21–36]. Indeed, the replacement of the fluorine atoms by other halogens in liquid crystals results in significant changes of their physico-chemical properties [1–3, 5, 9, 37–52]. The effects of lateral halogen substitution of liquid crystals have been studied in earlier publications [1, 2, 3, 9, 25–27, 53–57]. In this paper, the effect on physico-chemical properties of terminal and linking halogenation of achiral liquid crystals will be discussed, rationalized in terms of existing theories, and a comparison made with the corresponding hydrogenated and other well-known substitutents.

2. Mesomorphic properties

2.1. *Terminal substitution*

Many attempts have been made to understanding the influence of factors such as rigidity, linearity, size and polarizability of the terminal and linking groups on

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Table 1. Physico-chemical properties of halogen and hydrogen atoms and their derivatives [7–14].

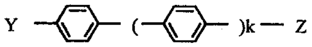
Property	X				
	F	Cl	Br	I	H
Electronegativity	3.98	3.16	2.96	2.66	2.20
Electron affinity/kcal mol^{-1}	79.5	83.3	72.6	70.6	17.7
Ionization potential/kcal mol^{-1}	401.8	299.0	272.4	241.2	313.6
van der Waals radii/Å	1.47	1.75	1.85	1.98	1.20
Atomic polarizability/$Å^3$	0.352	1.761	2.189	4.700	0.172
Anisotropy of polarizability of C–X bond $\times 10^{24}/cm^3$	1.10	1.59	2.16		0.22
Mean polarizability of $CH_3X/Å^3$	2.61	4.53	5.60	7.34	2.60
Mean polarizability of $CH_2X_2/Å^3$	2.73	6.57	8.65		
Mean polarizability of $CHX_3/Å^3$	2.88	8.51	11.79		
Mean polarizability of $CX_4/Å^3$	2.91	10.45			2.60
Mean polarizability of $C_6H_5X/Å^3$	9.86	11.86	12.93	15.20	9.96
Anisotropy of polarizability of C_5H_{11}–C_6H_{10}–C_6H_4–$C_6H_4X/Å^3$	19.7	20.1	20.6		18.5

mesophase stability [1–3, 41, 58–60]. However, the prediction and rationalization of LC mesomorphic properties still remain difficult problems [2, 3, 59, 61–63]. The aim of this section is therefore to define what relations can be established for LCs incorporating halogenated terminal and linking groups, even though these may be empirical. The phase transition temperatures of some halogenated LCs and the corresponding reference compounds are summarized in tables 2–14, where Cr, SmH, SmG, SmF, SmC, SmB, SmA, N and I are the crystalline, smectic H, smectic G, smectic F, smectic C, smectic B, smectic A, nematic and isotropic phases, respectively; X is an uncharacterized mesophase. Values given in parentheses related to monotropic phase transitions.

2.1.1. *One-ring derivatives*

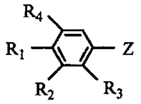
It has been demonstrated that neither 4-fluoro-, 4-chloro-, 4-bromo- and 4-iodo-benzene [64] nor 4-substituted benzene derivatives having polyfluorinated groups [18] show mesomorphic properties.

Mesophases can be observed for 1,4-disubstituted benzene derivatives having perfluoalkyl groups attached to the ring via connectors (compounds **2-1**, **2-3**, **2-6**, **2-7**, table 2, and [65–68, 74–78]). The importance of the structures of the connector and other substituents on mesomorphic properties is revealed by the phase transition temperatures of compounds **2-1** and **2-2**, **2-3** and **2-4**, and **2-7**–**2-9** presented in table 2, see also [65–68, 74]. Paticularly, increasing the length of the

Table 2. Mesomorphic properties of liquid crystals: 

Compound	Y	k	Z	Phase transitions/°C	Ref.
2-1	$C_6F_{13}C_2H_4O$	0	NO_2	Cr 22 SmA 41 I	[65]
2-2	$C_6F_{13}C_2H_4OOC$	0	NO_2	Cr 55 I	[66]
2-3	$C_6F_{13}C_2H_4O$	0	CN	Cr 40 SmA 45 I	[65]
2-4	$C_6F_{13}C_6H_{12}O$	0	CN	Cr 70 I	[67]
2-5	$C_4F_9C_8H_{16}O$	0	CN	Cr 46 I	[67]
2-6	$C_8F_{17}C_4H_8O$	0	CN	Cr 72 SmA 73 I	[67]
2-7	$C_{10}F_{21}C_2H_4O$	0	CN	Cr 83 SmB 104 SmA 112 I	[65]
2-8	$C_{10}F_{21}C_2H_4O$	0	F	Cr 74 I	[68]
2-9	$C_{10}F_{21}C_2H_4O$	0	CF_3	Cr 60 I	[68]
2-10	C_6F_{13}	1	H	Cr 69 I	[69]
2-11	$C_6F_{13}C_2H_4O$	1	H	Cr 81.4 SmE 96.1 SmA 105.5 I	[70]
2-12	C_6F_{13}	1	CN	Cr 101 I	[69]
2-13	C_6H_{13}	1	CN	Cr 13.5 N 28 I	[71]
2-14	$C_6F_{13}C_{11}H_{22}O$	1	CN	Cr 84 SmC 96 SmA 131 I	[72]
2-15	$C_8F_{17}C_5H_{10}O$	1	CN	Cr 97 SmC 106 SmA 162 I	[72]
2-16	$C_8F_{17}C_{10}H_{20}O$	1	CN	Cr 100 SmC SmC 121 SmA 150 I	[72]
2-17	$C_7F_{15}CH_2O$	1	CN	Cr 75 SmA 144 I	[72]
2-18	$C_8H_{17}O$	1	CN	Cr 54.5 SmA 67 N 80 I	[73]

Table 3. Mesomorphic properties of liquid crystals:



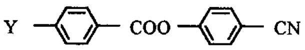
Compound	R_1	R_2	R_3	R_4	Z	Phase transitions/°C	Ref.
3-1	H	F	H	H	$COOC_2H_4C_8F_{17}$	Cr 27 SmB (7) I	[68]
3-2	H	H	Cl	H	$COOC_2H_4C_8F_{17}$	Cr 17 I	[68]
3-3	$C_6H_{13}O$	Br	H	H	$COOC_2H_4C_8F_{17}$	SmB 30 I	[68]
3-4	$C_6H_{13}O$	NO_2	H	H	$COOC_2H_4C_8F_{17}$	Cr 44 SmB 49 SmA 51 I	[68]
3-5	$C_6H_{13}O$	Br	H	Br	$COOC_2H_4C_8F_{17}$	Cr 52 I	[68]
3-6	$C_6H_{13}OOC$	H	H	H	$OC_2H_4C_8F_{17}$	Cr 65 I	[74]
3-7	$C_6H_{13}OOC$	H	Br	H	$OC_2H_4C_8F_{17}$	Cr 58 SmA (45) I	[74]
3-8	$C_6H_{13}OOC$	H	NO_2	H	$OC_2H_4C_8F_{17}$	Cr 70 SmA (68) I	[74]
3-9	C_4H_9OOC	H	H	H	$OC_2H_4C_8F_{17}$	Cr 70 SmA (52) I	[74]
3-10	C_4H_9OOC	H	Br	H	$OC_2H_4C_8F_{17}$	Cr 75 SmA (52) I	[74]
3-11	C_4H_9OOC	H	NO_2	H	$OC_2H_4C_8F_{17}$	Cr 73 SmB (54) SmA (72) I	[74]
3-12	C_2H_5OOC	H	H	H	$OC_2H_4C_8F_{17}$	Cr 80 SmA (70) I	[74]
3-13	C_2H_5OOC	H	Br	H	$OC_2H_4C_8F_{17}$	Cr 73 SmA (56) I	[74]
3-14	C_2H_5OOC	H	NO_2	H	$OC_2H_4C_8F_{17}$	Cr 95 SmA (81) I	[74]

Table 4. Mesomorphic properties of liquid crystals:

Compound	Y	Z	Phase transitions/°C	Ref.
4-1	$C_8H_{17}O$	$COOCH_2C_2F_5$	Cr 48 SmC 68 SmA 84 I	[76]
4-2	$C_8H_{17}O$	$COOCH_2C_2F_4H$	Cr 76 SmC (37) SmA (58) I	[76]
4-3	$C_8H_{17}O$	$COOC_2H_4C_4F_9$	Cr 71 SmC 109 SmA 111 I	[76]
4-4	$C_8H_{17}O$	$COOC_6H_{13}$	Cr 51 SmA 69 I	[76]
4-5	$C_8H_{17}O$	$COOCH_2C_6F_{13}$	Cr 71 SmC 107 SmA 120 I	[76]
4-6	$C_8H_{17}O$	$COOC_2H_4C_6F_{13}$	Cr 88 SmC 122 SmA 129 I	[76]
4-7	$C_4F_9C_4H_8O$	$COOC_2H_4C_6F_{13}$	Cr 126.3 SmC (114.7) SmA (118.5) I	[93]
4-8	$C_4F_9C_5H_{10}O$	$COOC_2H_4C_6F_{13}$	Cr 92.8 SmC 114.7 I	[93]
4-9	$C_4F_9C_3H_6O$	$COOC_2H_4C_6F_{13}$	Cr 104.1 SmC 115.8 I	[93]
4-10	$C_4F_9C_2H_4OOC$	OC_8H_{17}	Cr 87 SmA 96 I	[77]
4-11	$C_6H_{13}OOC$	OC_8H_{17}	Cr 57 I	[77]
4-12	CF_3	OC_5H_{11}	Cr 79 I	[94]
4-13	CH_3	OC_5H_{11}	Cr 61 Sm 63 I	[94]
4-14	CF_3O	OC_5H_{11}	Cr 47 Sm 92 I	[94]
4-15	CHF_2O	OC_5H_{11}	Cr 61 N (56) I	[94]
4-16	CH_3O	OC_5H_{11}	Cr 68 N 73 I	[94]
4-17	C_2F_5O	OC_5H_{11}	Cr 76 Sm 107 I	[94]
4-18	C_2H_5O	OC_5H_{11}	Cr 94 N 102 I	[94]

connector, from ethyloxy to hexyloxy, results in the disappearance of the mesophase (compounds **2-3** and **2-4**). In terms of the ratio between the perfluorocarbon and hydrocarbon parts of the substituents, an increase in the fluorination content of the polyfluorinated group, having twelve carbon atoms, leads to an increase in the melting temperatures {crystal–smectic or crystal–nematic phase transition temperatures} (compounds **2-4**–**2-7**, table 2). The appearance of the smectic phase and an increase of its thermostability (smectic–isotropic phase transition temperature) have been recorded for only perfluorooctyl and longer derivatives (compounds **2-6** and **2-7**, and [67]). The importance of the relative positions of the perfluoroalkyl group and other substituents to the mesomorphic properties of one-ring benzene derivatives has been shown in [65–68, 74–78]. The introduction of halogens and fluorinated groups into the molecular structure of perfluoroalkyl-substituted benzenes may lead to smectic phases (compounds **3-1**, **3-3**, **3-6** and **3-7**, table 3), maintain the same smectic thermostability (compounds **3-9** and **3-10**), decrease the clearing temperatures {smectic–isotropic or nematic–isotropic phase transition temperatures} (compounds **3-12** and **3-13**), and suppress mesomorphism (compounds **2-8**, **2-9**, **3-2**, tables 2, 3) in comparison with those of the corresponding hydrogenated derivatives (when it is applicable). As

Table 5. Mesomorphic properties of liquid crystals:



Compound	Y	Phase transitions/°C	Ref.
5-1	C_3F_7	Cr 93 I	[97]
5-2	C_4F_9	Cr 82.5 Sm (80) I	[97]
5-3	C_5F_{11}	Cr 100 Sm 123 I	[97]
5-4	C_6F_{13}	Cr 100 Sm 124 I	[98]
5-5	C_7F_{15}	Cr 104 Sm 136 I	[97]
5-6	$CF_3C_2H_4$	Cr 99 Sm (57) I	[99]
5-7	$CF_3C_3H_6$	Cr 74 I	[99]
5-8	C_3H_7	Cr 103.5 N (51.4) I	[100]
5-9	C_4H_9	Cr 66.1 N (41.4)	[100]
5-10	C_5H_{11}	Cr 64.4 N (55.4) I	[101]
5-11	C_6H_{13}	Cr 44.4 N 48.6 I	[101]
5-12	C_7H_{15}	Cr 44 N 56.5 I	[101]
5-13	C_4F_9O	Cr 80 Sm 128 I	[98]
5-14	$C_5F_{11}O$	Cr 143 Sm (136) N (142) I	[98]
5-15	$C_7F_{15}O$	Cr 104 Sm 128 I	[98]
5-16	C_4H_9O	Cr 92 N 104 I	[100]
5-17	$C_5H_{11}O$	Cr 87 N 96 I	[100]

can be seen from table 3, decreasing the length of the R_1 group ($C_nH_{2n+1}OOC$) changes the efficiency of the R_3 group (H, Br, NO_2) attached to the same benzene ring (compounds **3-6**–**3-14**):

$$n = 6 \quad T_{clp} \rightarrow R_3: \mathrm{H} < \mathrm{Br} < \mathrm{NO_2}$$

$$n = 4 \quad T_{clp} \rightarrow R_3: \mathrm{H} \approx \mathrm{Br} < \mathrm{NO_2}$$

$$n = 2 \quad T_{clp} \rightarrow R_3: \mathrm{Br} < \mathrm{H} < \mathrm{NO_2}.$$

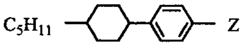
These results and the phase transition temperatures presented in tables 2 and 3 for compounds **2-7**–**2-9**, **3-3** and **3-4**, show that the halogens and fluorinated groups exhibit lower thermal efficiency than the strongly polar NO_2 and CN groups in one-ring perfluoroalkyl-substituted derivatives.

From table 3 it is seen that increasing the quantity of bromine atoms introduced into the molecular structure of perfluoroalkyl-substituted benzenes suppresses mesomorphic properties (compounds **3-3** and **3-5**, and [68]), which is similar to results reported for other liquid crystalline derivatives [21]. It seems that the mesomorphic properties of one-ring halogenated derivatives are strongly influenced by its entire molecular structure, while fluorophilic [49, 74] and fluorophobic [65–68, 74–78] interactions between the perfluoroalkyl groups and the residual hydrocarbon moiety play very important roles in the formation of the mesophases. Similar results have been found for other perfluoro(alkoxy)alkylated one-ring derivatives [65–68, 74–84].

2.1.2. *Two-ring derivatives*

As in the case of 4-halogenobenzenes discussed in the previous paragraph, 4-halogen as well as 4-perfluoroalkyl substitutions of the biphenyl fragment do not change its non-mesomorphic character (compound **2-10**, table 2, and [64, 69]. Such non-mesomorphic behaviour has been reported for the corresponding 4-alkylbiphenyls [85]. The introduction of the connector between the perfluorohexyl group and the biphenyl core can create smectic mesophases (in contrast to the non-mesomorphic

Table 6. Physico-chemical properties of liquid crystals:



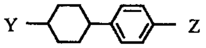
Compound	Z	Phase transitions/°C	$\Delta\varepsilon$[a]	Δn[a]	v[a]/$mm^2\,s^{-1}$	Ref.
6-1	F	Cr 31 I	3.2	0.024	3	[129, 130]
6-2	$OCHF_2$	Cr 1 N (− 17) I	7.6	0.058	7	[23]
6-3	OCF_3	Cr 14 I	7.1	0.046	4	[23]
6-4	CF_3	Cr 21 I	10.9	0.040	9	[23]
6-5	$SCHF_2$	Cr 7 I	7.2	0.055	14	[104]
6-6	OCH_3	Cr 41 N (31) I	− 0.5	0.090	8	[131]
6-7	$COCHF_2$	Cr 39 I	11.1	0.076	21	[104]
6-8	$COCF_3$	Cr 7 N (− 24) I	15.5	0.078	15	[104]
6-9	$COCF_2C_3H_7$	Cr 20 SmB 33 N 53.9 I	5.7	0.096	17	[104]
6-10	$CHFCF_2CH_3$	Cr 13 I				[132]
6-11	CF=CHF (cis)	Cr 30 N 61.9 I				[107]
6-12	$CH{=}CF_2$	Cr 10 N 60 I				[31]
6-13	$OCF_2CH{=}CH_2$	Cr 29 SmB (9) N (20.3) I		0.066[b]		[133]
6-14	CF_2CN	Cr 71 I	11.6		8	[134]
6-15	CH_2CN	Cr 53 X (19) I[c]				[135]
6-16	CN	Cr 30 N 55 I	12.2[d]	0.119[d]	21.5[d]	[136, 137]

[a,b] Extrapolated from 10 wt % solution in ZLI-1132 and ZLI-4792, respectively, measured at 20°C.

[c] X is an unknown mesophase.

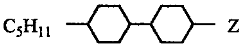
[d] T_{meas} = 22°C.

Table 7. Mesomorphic properties of liquid crystals:



Compound	Y	Z	Phase transitions/°C	Ref.
7-1	C_5H_{11}	Cl	Cr 29.7 I	[138]
7-2	C_5H_{11}	$COCH_3$	Cr 66.7 I	[139]
7-3	C_5H_{11}	COC_4H_9	Cr 40 Sm 52.3 N 57.9 I	[139]
7-4	C_5H_{11}	C_3H_7	Cr − 12.7 N − 11.2 I	[109]
7-5	$CHF_2C_4H_8$	CN	Cr 29 N 34 I	[140]
7-6	C_3H_7	CH=CHF	Cr 24 N 70 I	[31]
7-7	C_3H_7	$CH{=}CF_2$	Cr 7 N 48 I	[31]
7-8	FC_4H_8	CN	Cr 42.6 N (33.7) I	[52]
7-9	ClC_4H_8	CN	Cr 64.9 N (31) I	[52]
7-10	BrC_4H_8	CN	Cr 63.5 I	[52]
7-11	IC_4H_8	CN	Cr 71 I	[52]
7-12	C_4H_9	CN	Cr 41 N (40.5) I	[136]
7-13	$CHF{=}CHC_2H_4$	CN	Cr 74 N (68) I	[31]
7-14	$CF_2{=}CHC_2H_4$	CN	Cr 12 N 28 I	[31]
7-15	$CH_2{=}CHC_2H_4$	CN	Cr 49.5 N 52.5 I	[141]
7-16	$FC_2H_4CH{=}CH$	CN	Cr 38.6 N 51.9 I	[142]
7-17	$CF_3CH_2CH{=}CH$	CN	Cr 46.1 I	[142]
7-18	$C_2H_5CH{=}CH$	CN	Cr 45.1 N 51.8 I	[141]

Table 8. Physico-chemical properties of liquid crystals:

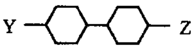


Compound	Z	Phase transitions/°C	$\Delta\varepsilon^a$	Δn^a	$v^a/mm^2\ s^{-1}$	Ref.
8-1	$OCHF_2$	Cr < 20 I	2.3	0.040		[143]
8-2	CHF_2	Cr 29 X 32.1 I			14	[144]
8-3	CH_2CHF_2	Cr − 1 X 82 I		0.040	11	[144]
8-4	$C_2H_4CF_3$	Cr 50 X 75 I				[145]
8-5	$CF_2C_2H_5$	Cr 27.5 SmB 89.2 I				[146]
8-6	CH_2OCF_3	SmB 55 I				[147]
8-7	C_2H_4Br	Cr 46 Sm 47.8 N 67.9 I				[109]
8-8	$COOCH_2CF_3$	Cr 41 SmB 65 I	2.7	0.038	16	[104]
8-9	$CH{=}CF_2$	Cr − 2 SmB 49 N 62 I				[31]
8-10[c]	CF=CHF (*trans*)	Cr 33 SmB 37 I				[148]
8-11[c]	CF=CHF (*cis*)	Cr 20 SmB 23 N 70 I				[148]
8-12	$OCH{=}CF_2$	Cr 34 N (31) I	4.6^b	0.045^b		[149]
8-13	$CH_2OCH{=}CF_2$	Cr − 8 SmB 72 I		0.051^b	11^b	[150]
8-14	OCH_2CH_2F	Cr 53.2 SmB 68.1 I				[146]
8-15	OCH_3	Cr 12 SmB 29 N 37 I				[151]
8-16	C_2H_5	Cr − 8 Sm 76.1 I				[109]
8-17	CN	Cr 60 Sm_1 (43) Sm_2 (52) N 85 I	4.5	0.061	60	[130, 152]

[a,b] Extrapolated from 10 wt % solution in ZLI-1132 and ZLI-4792, respectively, measured at 20°C.
[c] Taken from the figure in [148].

behaviour of the corresponding hydrocarbon derivatives [86]), with the phase transition temperatures depending on the structure of the connectors and on the ratio between the perfluorocarbon and hydrocarbon parts of the substituents (compound **2-11**, table 2, and [70, 86–88]).

As can be seen from table 2, 4-perfluorohexyl-4′-cyanobiphenyl **2-12** exhibits non-mesomorphic behaviour in comparison with the low melting nematic phase of its hydrocarbon analogue **2-13**; mesophases appear for compounds having the connectors introduced between the perfluorohexyl group and 4′-cyanobiphenyl fragment (compounds **2-14**–**2-17**, table 2). Similar results have been reported for weakly polar 4,4′-disubstituted biphenyls having perfluoro(alkoxy)alkyl groups [89–92]. As was observed above for one-ring benzene derivatives, an increase in the length of the connector leads to a decrease in the clearing point (compounds **2-15** and **2-16**, and [90]). However, replacement of the terminal cyano group by an alkoxy group, and changing the structure of the connector, can lead to the opposite behaviour of the clearing temperatures for biphenyls [89] and phenyl benzoates (compounds **4-5** and **4-6**, table 4, [76, 77]). The data collated in table 2 reveal that partial fluorination of the terminal hydrocarbon groups results in an

Table 9. Mesomorphic properties of liquid crystals: 

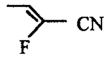
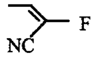
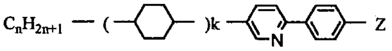
Compound	Y	Z	Phase transitions/°C	Ref.
9-1	C_5H_{11}	C_3H_7	Cr 15.6 Sm 95.6 I	[34]
9-2	C_5H_{11}	OC_2H_5	Cr 35 SmB 56 N 63 I	[151]
9-3	C_5H_{11}	$COOC_2H_5$	Cr 23.1 Sm 80.6 I	[153]
9-4	C_5H_{11}	CH_2OCH_3	Cr 19.6 Sm 73.4 I	[153]
9-5	C_5H_{11}	$CH{=}CH_2$	Cr − 8 SmB 50 N 63.0 I	[148]
9-6	C_3H_7	CF_3	Cr 43 I	[154]
9-7	C_3H_7	$OCHFCF_3$	Cr 51 Sm (45) I	[155]
9-8	C_3H_7	$OC_3H_6CF_3$	Cr 10 SmB 47 I	[156]
9-9	C_3H_7	CF_2OCH_3	Cr 51.5 SmB 90.8 I	[146]
9-10	C_3H_7	$OCOCF_3$	Cr 37.7 SmB 56.7 I	[157]
9-11	C_3H_7	$OCOCHF_2$	Cr 68.9 I	[157]
9-12	C_3H_7		Cr 38.4 SmB 65.6 N 124.1 I	[158]
9-13	C_3H_7		Cr 51.3 I	[158]
9-14	C_3H_7	CH_3	Cr 7 Sm 25.7 I	[109]
9-15	C_3H_7	OC_2H_5	Cr 49 N (30) I	[151]
9-16	C_3H_7	OC_4H_9	Cr 32 SmB 74 I	[151]
9-17	C_3H_7	CH_2OCH_3	Cr 44.8 Sm 51 N 52 I	[153]
9-18	C_3H_7	$CH{=}CHCN$	Cr 38.9 Sm_3 57.4 Sm_2 59.3 Sm_1 65.5 N 162.2 I	[158]

Table 10. Physico-chemical properties of liquid crystals: 

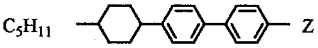
Compound	*n*	*k*	Z	Phase transitions/°C	$\Delta\varepsilon^a$	Δn^a	$v^a/mm^2\ s^{-1}$	k_p, 40°C	Ref.
10-1	5	0	F	Cr 28.1 I	9.8	0.074		0.6593	[22, 159]
10-2	5	0	Br	Cr 84 X (66) I					[160]
10-3	5	0	$OCHF_2$	Cr 26 Sm 43.6 I	15.9	0.125	12	0.5929	[22, 159]
10-4	5	0	OCF_3	Cr 18.6 SmB 38.5 SmA 52.4 I	11.8	0.074			[22]
10-5	5	0	$SCHF_2$	Cr 2.5 I		0.133		0.5838	[22, 159]
10-6	5	0	OCF_2Cl	Cr 36 I					[24]
10-7	5	0	C_6F_{13}	Cr< 20 SmB 81.5 SmA (76.5) I		0.142			[22, 161]
10-8	5	0	C_6H_{13}	Cr 15 SmA 33 I					[22]
10-9	5	0	CN	Cr 33.6 N 43.5 I	17.8^b	0.214	50	0.6538	[22, 162]
10-10	7	0	OC_7F_{15}	Cr 53.1 SmA 111.7 I					[22]
10-11	7	0	OC_7H_{15}	Cr 24 SmH 31.5 SmG 40.3 SmF 53 SmC 76.6 I					[22]
10-12	4	1	$OCHF_2$	Cr 57.1 Sm 135.7 N 165.3 I	13.8	0.154			[22]
10-13	4	1	OCF_3	Cr 35.1 Sm 149.2 N 154.8 I	10.6	0.123			[22]
10-14	4	1	$SCHF_2$	Cr 41.5 Sm 95 N 119 I	14.1	0.144			[159]
10-15	4	1	OCF_2Cl	Cr 79.5 Sm 121.7 N 130.3 I	12.2	0.134			[24]
10-16	4	1	CN	Cr 124 N 228 I	17.6	0.232			[159, 162]

[a] Extrapolated from 10 wt % solution in ZLI-1132 at 20°C.
[b] $\tau = T_{meas}/T_{N\text{-}I} = 0.95$; T_{meas}, $T_{N\text{-}I}$/K.

increase in melting and clearing temperatures and the disappearance of the nematic phases (compounds **2-17** and **2-18**).

An increase in the clearing temperatures, due to the increase of the fluorine content of terminal groups, has been demonstrated for weakly polar biphenyls [89, 95, 96] and phenyl benzoates (compounds **4-1** and **4-2**; **4-3** and **4-4**; **4-10** and **4-11**; **4-14** and **4-16**, **4-15**; **4-17** and **4-18**; **5-2** and **5-7**, **5-9**; **5-3** and **5-10**; **5-4** and **5-11**; **5-5** and **5-12**; **5-13** and **5-17**; **5-14** and **5-18**; tables 4, 5, and [76, 77, 91]). It is important to note that increasing the fluorination content of the terminal groups of phenyl benzoates can lead to a lowering of their nematic thermostability {nematic–isotropic phase transition temperature} (compounds **4-15** and **4-16**) and to the disappearance of the mesophase (compounds **4-12** and **4-13**, **5-1** and **5-8**, **5-7** and **5-9**); while the melting temperatures show an increase (compounds **4-3** and **4-4**; **4-10** and **4-11**; **4-12**

Table 11. Physico-chemical properties of liquid crystals:



Compound	Z	Phase transitions/°C	$\Delta\varepsilon^{a}$	Δn^{a}	ν^{a}/mm^{2} s^{-1}	k_{p}^{e}	Ref.
11-1	F	Cr 94.4 N 152.9 I	4.6^{b}	0.098^{d}	24.7^{c}	0.6502	[30, 14, 171]
11-2	Cl	Cr 135.7 N 185 I		0.125^{d}		0.6700	[14, 171]
11-3	Br	Cr 153.4 N 192.7 I		0.138^{d}		0.6300^{f}	[14, 171]
11-4	$OCHF_2$	Cr 69 Sm 119.6 N 167.5 I	9.7	0.154	28		[22]
11-5	OCF_3	Cr 43 SmB 128 N 147.4 I	8.9	0.140	16		[23]
11-6	CF_3	Cr 123 N 124.2 I	12.9	0.159	32		[23]
11-7	$SCHF_2$	Cr 56.2 Sm 94.7 N 114 I	11.4	0.174			[22]
11-8	CHF_2	Cr 122 N 161.8 I	4.4				[105]
11-9	SCF_3	Cr 60 SmB 78 N 105.2 I	9.4	0.149	39		[104]
11-10	$COCHF_2$	Cr 80 N 158 I	10.2	0.200	83		[104]
11-11	$COCF_3$	Cr 70 N 141.2 I	17.7	0.196	60		[104]
11-12	$COCF_2CH_3$	Cr 52 SmB 140 SmA 169 N 190.7 I	8.5		54		[104]
11-13	$COOCH_2CH_3$	Cr 90 SmB 128 SmA 165 N 170.5 I	7.6	0.162	78		[104]
11-14	$SOCHF_2$	Cr 102 N 108.5 I	16.3	0.151			[104]
11-15	$SOOCHF_2$	Cr 119 I	13.1	0.155			[104]
11-16	$SOCF_3$	Cr 123 I	12.5	0.158			[104]

[a] Extrapolated from 10 wt % solution in ZLI-1132 at 20°C.

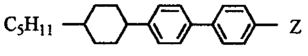
[b,c] Extrapolated from 20 wt % solution in the mixture of 3,4-difluoroderivatives, measured at 25 and 20°C, respectively.

[d] $\tau = 0.95$.

[e] $T_{\text{meas}} = 150$°C.

[f] Extrapolated to $T = 150$°C.

Table 12. Physico-chemical properties of liquid crystals:



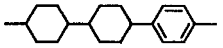
Compound	Z	Phase transitions/°C	$\Delta\varepsilon^{a}$	Δn^{a}	ν^{a}/mm^{2} s^{-1}	k_{p}^{c}	Ref.
12-1	$CF_2CF_2CH_3$	Cr 147 I	5.8				[132]
12-2	$CHFCF_2CH_3$	Cr 147 I	7.5		100		[33, 132]
12-3	$CH_2CF_2CH_3$	Cr 148 I	6.9		76		[33, 132]
12-4	$CF_2CH_2CF_3$	Cr 86 SmB 113 I	10.7^{b}	0.133^{b}			[172]
12-5	CH_2CHFCH_3	Cr 43 SmB 146 N 160.2 I	6.5				[132]
12-6	OCH_2CHF_2	Cr 94 SmB 168 SmA 194 N 209.3 I	4.5^{b}				[173]
12-7	OCF_2CHFCF_3	Cr 176.5 SmB 181.5 I					[174]
12-8	$OCH_2CH{=}CF_2$	Cr 53 SmB 162 SmA 203 N 205.2 I		0.185^{b}			[133]
12-9	$OCF_2CH{=}CH_2$	Cr 178 N (177.2) I		0.166^{b}			[133]
12-10	$CH{=}CF_2$	Cr 56.7 Sm 184 N 232 I					[175]
12-11	$COCF_2Cl$	Cr 52 N 124 I	16.5	0.185	98		[104]
12-12	CF_2CN	Cr 59 N (47.7) I	12.9		46		[134]
12-13	C_3H_7	Cr 29 SmA 160 N 170 I	0.4		24		[33, 176]
12-14	OCH_3	Cr 80 N 165 I			70		[129]
12-15	CH_3	Cr 98 Sm 123 N 178 I					[177]
12-16	H	Cr 58 Sm 81.7 N 98 I					[171]
12-17	CN	Cr 96 N 222 I	17	0.210	90	0.6235	[129, 171, 178]

[a,b] Extrapolated from 10 wt % solution in ZLI-1132 and ZLI-4792, respectively, measured at 20°C.

[c] $T_{\text{meas}} = 150$°C.

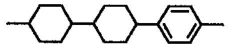
and **4-13**; **5-2** and **5-7**, **5-9**; **5-3** and **5-10**; **5-4** and **5-11**; **5-5** and **5-12**; **5-14** and **5-18**; and [76, 77, 89, 91]) and decrease (compounds **4-1** and **4-2**; **4-14**–**4-16**; **4-17** and **4-18**; **5-1** and **5-6**, **5-8**; **5-13** and **5-17**; tables 4, 5, and [95, 96]), with increasing of fluorination content.

It has been shown that the terminal 4′-substitution of 4-*n*-pentylbiphenyl by iodine and short halogenated groups (OCF_3, SCF_3, $COCF_3$, OCH_2CF_3, CHF_2, $CHFCF_3$, CF=CHCl, C_2H_4I, C_2H_4Cl) does not create mesophases [103–109], in contrast to the nematic and smectic phases, with low melting and clearing points, exhibited by the corresponding 4′-cyano [71] and 4′-alkyl derivatives [110], respectively. As in the case of cyano derivatives [111], it has been shown that the introduction of the acetylenic bond between the terminal halogen substituent (Br, I) and 4-*n*-pentylbiphenyl significantly increases the mesophase thermostability [112].

Table 13. Physico-chemical properties of liquid crystals: C_3H_7  X

Compound	X	Phase transitions/°C	$\Delta\varepsilon$[a]	Δn[a]	ν[a]/$mm^2\,s^{-1}$	Ref.
13-1	F	Cr 54.1 Sm 96.6 N 155.2 I	4[b]	0.097[b]	16[b]	[30, 179]
13-2	Cl	Cr 70 Sm 79 N 193 I	6[b]	0.125[b]	24[b]	[179]
13-3	I	Cr 119 Sm 139.2 N 189.2 I				[180]
13-4	$OCHF_2$	Cr 50.8 Sm 69.2 N 172.2 I	10.5	0.114	23	[22, 23]
13-5	OCF_3	Cr 38 SmB 69 N 153.7 I	9.2	0.088	16	[23]
13-6	CF_3	Cr 133 I	13.2	0.02	26	[23]
13-7	SCF_3	Cr 51 N 109.5 I	8.6	0.100	29	[104]
13-8	SF_5	Cr 121 I	11.6[b]	0.094[b]		[35]
13-9	OCF_2Cl	Cr 82 N 133 I	7.5	0.100		[24]
13-10	$COCF_2CH_3$	Cr 92 N 197.1 I	7.1	0.146	56	[104]
13-11	$C_2F_4CH_3$	Cr 162 I				[33]
13-12	$CH_2OCH_2CF_3$	Cr 32.1 SmB 167.4 I				[181]
13-13	$CH_2OCH_2CF_2CHF_2$	Cr 34 SmB 148.7 I				[181]
13-14	$CH{=}CF_2$	Cr 51 Sm 88.6 N 233 I				[175]
13-15	$CF{=}CHCl$	Cr 98 N 271.9 I				[107]
13-16	CH_3	Cr 64.6 Sm 109.7 N 179.8 I	0.2	0.111	22	[131, 182]
13-17	CN	Cr 73.1 Sm 81.1 N 242.5 I	12.0[b]	0.182[b]	94[b]	[179, 180]

[a,b] Extrapolated from 10 wt % solution in ZLI-1132 and ZLI-4792, respectively, measured at 20°C.

Table 14. Mesomorphic properties of liquid crystals: Y  Z

Compound	Y	Z	Phase transitions/°C	Ref.
14-1	C_3H_7	H	Cr 75.9 Sm 91.8 N 100.4 I	[182]
14-2	C_3H_7	OCH_3	Cr 79.2 Sm 128.4 N 211.5 I	[182]
14-3	C_3H_7	C_3H_7	Cr 21 SmB 178 I	[33]
14-4	C_3H_7	$N(CH_3)CF_3$	Cr< 20 SmB 173 I	[183]
14-5	C_3H_7	$N(CH_3)CH_3$	Cr 59 Sm 189 I	[183]
14-6	C_5H_{11}	$C_2F_4CHF_2$	Cr 43 SmB 88 SmC 107 SmA 130 I	[33]
14-7	C_5H_{11}	C_3F_7	Cr 127 N (126) I	[33]
14-8	C_5H_{11}	C_3H_7	Cr 48.6 Sm 181 I	[182]
14-9	CH_3CHFCH_2	F	Cr 86 N 152 I	[184]
14-10	$CF_2{=}CH$	CH_3	Cr 73.2 Sm 93.1 N 170.5 I	[185]
14-11	$ClCH{=}CH$	CH_3	SmB 99.6 N 242.2 I	[186]
14-12	$CH_2{=}CH$	CH_3	Cr 63.5 N 159 I	[185]
14-13	$ClCH{=}CH$	F	Cr 103.3 N 204 I	[187]
14-14	$CH_2{=}CH$	F	Cr 85 N 145 I	[36]
14-15	$ClCH{=}CH$	Cl	Cr 211 N 266.5 I	[187]
14-16	$CH_2{=}CH$	Cl	Cr 102.4 N 179.5 I	[188]
14-17	$ClCH{=}CH$	Br	Cr 185.8 N 265.2 I	[187]
14-18	$BrCH{=}CH$	Br	Cr 207 N 267.8 I	[187]

As is evident from table 5, the perfluoroalkylation of cyanophenyl benzoates creates smectic mesophases with an almost suppressed odd–even effect in the clearing temperatures in comparison with those of the corresponding nematic alkyl-substituted cyanophenyl benzoates (compounds **5-1**–**5-5** and **5-8**–**5-12**, table 5, and [69, 97, 98, 100–102, 113]):

$$X = \mathrm{F} \quad T_{\mathrm{clp}} \rightarrow C_nX_{2n+1}: C_3F_7 < C_4F_9 < C_5F_{11} < C_6F_{13} < C_7F_{15}$$

$$X = \mathrm{H} \quad T_{\mathrm{clp}} \rightarrow C_nX_{2n+1}: C_4H_9 < C_6H_{13} < C_3H_7 < C_5H_{11} < C_7H_{15}.$$

The perfluoroalkoxylation of the corresponding cyanophenyl benzoates also promotes the formation of smectic phases and its effect on the odd–even dependence of the clearing points is less disturbing (compounds **5-13**–**5-15**, **5-16**, **5-17** and [98, 100]).

Considering the effects of perfluoro(alkoxy)alkylation and polyfluoro(alkoxy)alkylation in other 1,4-phenylene derivatives containing linking groups, we can point out that increasing the fluorination content of their terminal groups creates, in many cases, smectic phases and leads to decreasing [94, 99, 114–117] or increasing [26, 46, 76, 77, 91, 94, 97–99, 100–102, 114, 118–121] clearing temperatures, and to decreasing [46, 94, 97–100, 114, 116] or increasing [26, 46, 76, 77, 91, 94, 97–102, 114–118, 120, 121] melting points.

It has been shown that the terminal halogenation of 4-octyloxy-*N*-(4-substituted benzylidene)aniline results in the formation of mesophases exhibiting the following orders of increasing the melting (T_m) and clearing temperatures (T_{clp}) [39]:

$$T_m \rightarrow H < CN < F < Cl < Br < I$$

$$T_{clp} \rightarrow Cl < CN < Br < I.$$

The low nematic thermostability of 4-octyloxy-*N*-(4-cyanobenzylidene)aniline, compared with those of the corresponding halogen-substituted derivatives, is difficult to explain in terms of the theory of Maier and Saupe, stating that the nematic–isotropic phase transition temperature is proportional to the anisotropy of polarizability of the molecules forming the nematic phase [122]. In such a case, the cyano derivative, having increased the value of the anisotropy of polarizability, should exhibit a higher clearing temperature in comparison with those of the corresponding halogen-substituted derivatives showing lower values of anisotropy of polarizability [41, 14]. Also, a low melting temperature of the cyano derivative (in comparison with that of the corresponding halogen-substituted derivatives) does not support the suggestion that increasing the polarity of the terminal substituents [39, 123] should increase the melting temperature [124].

It has been demonstrated that perfluoroalkylation of both achiral non-symmetrical terminal substituents attached to the biphenyl core leads to the formation a ferroelectric repolarizable mesophase [125–127]. Symmetrical perfluoro(polyfluoro)alkoxylation in both terminal positions of azoxybenzenes does not create mesophases, in comparison with the higher melting mesophases exbited by the corresponding symmetrical di-alkoxy derivatives [128]. Non-symmetrical perfluoro-(polyfluoro)alkoxy–alkoxy azoxybenzene derivatives exhibit mostly smectic character of their mesophases [128], as was observed above for many other liquid crystalline derivatives. Similar effects have been reported for non-mesomorphic 4,4′-bis-difluoromethoxy- and 4,4′-bis-trifluoro-methoxy-substituted benzaldazines, in comparison with the corresponding bis-methoxy derivative exhibiting a higher melting nematic phase [121]. It should be mentioned that non-symmetrical perfluoroalkylation in both terminal positions of phenylbenzoates results in a decrease in clearing points and increase in melting temperatures (compounds **4-6** and **4-7**, table 4 and [76, 77, 93]; while non-symmetrical polyfluorination or perfluoroalkylation–perfluoroalkoxylation in both terminal positions of Shiffs bases results in the disappearance of the mesophases [118] compared with those of the corresponding hydrocarbon derivatives. Increasing the length of the connector between the second perfluoroalkyl group and the molecular core in phenyl benzoates may increase (compounds **4-9** and **4-7** and [93]) or decrease (compounds **4-9**, **4-7** and **4-8**, table 4 and [93]) the clearing and melting points.

The thermal data collated in tables 6 and 7 reveal that the terminal substitution of *trans*-4-*n*-pentylcyclohexylbenzene by halogens and fluorinated groups does not create mesophases (compounds **6-1**, **6-3**–**6-5**, **6-7**, **6-10**, **7-1**; except compounds **6-2** and **6-8** showing the monotropic nematic phases at negative temperatures). Increasing the length of the fluorinated groups, or using fluoroalkenyl groups, may enhance the mesomorphic properties (compounds **6-9**, **6-11**–**6-13**, **7-6**, **7-7**). The corresponding derivatives having terminal hydrocarbon groups usually exhibit the same non-mesomorphic behaviour with higher melting points (compounds **6-7**, **6-8** and **7-2**) or mesophases with higher melting and clearing temperatures (compounds **6-2**, **6-3** and **6-6**; **6-9** and **7-3**) or mesophases with lower melting temperatures (compounds **6-10** and **7-4**). The introduction of the CF_2CN group results in the disappearance of the nematic phase, while a corresponding CH_2CN substitution leads to the creation of a monotropic phase with a lower melting point than that of the corresponding cyano derivative (compounds **6-14**–**6-16**). Partial fluorination of the alkyl group in (*trans*-4-alkylcyclohexyl)-1-cyanobenzene may lead to a decrease in melting and clearing temperatures (compounds **7-5** and **6-16**, tables 6, 7) or to an increase in melting and decrease in clearing points (compounds **7-8** and **7-12**, table 7). These findings show the importance of the structure of the terminal group and its fluorination content on the mesomorphic properties of fluoroalkylated LCs. Similar results have been found for the other halogenated LCs **7-9**–**7-12** presented in table 7.

Interestingly, the effect of fluorination of the alkenyl groups of the *trans*-1,4-cyclohexylene cyano derivatives on their mesomorphic properties depends on the fluorination content, position of fluorine atoms and the structure of the alkenyl groups. So far the introduction of one fluorine atom increases the nematic thermostability and may lead to increasing (compounds **7-13** and **7-15**) or decreasing (compounds **7-16** and **7-18**) melting points, while the introduction of two and more fluorine atoms decreases the melting and clearing temperatures (compounds **7-6** and **7-7**, **7-14** and **7-15**) or results in the disappearance of the mesophase with an increase of the melting point (compounds **7-17** and **7-18**, table 7). As was observed above for perfluoroalkyl-substituted cyanophenyl benzoates, perfluoroalkylation of cyanophenyl esters of cyclohexanecarboxylic acid creates only smectic phases exhibiting higher clearing and melting points than those of the corresponding alkyl-substituted derivatives [97].

In comparison with the above-considered biphenyls and phenylcyclohexanes, the effect on mesomorphic properties of terminal substitution of *trans*-4-*n*-pentyl- or propyl-bicyclohexyls by halogenated groups is more pronounced: in most cases we see the creation of mesophases exhibiting mainly smectic character (compounds **8-5**–**8-10**, **8-13**, **8-14**, **9-7**–**9-10**, except **8-1**, **9-6**, **9-11**, tables 8, 9). The replacement of the hydrogen atoms by fluorine and bromine atoms in the terminal substituents decreases (compounds **8-1** and **8-15**; **8-4**, **8-5** and **9-1**; **8-6** and **9-4**; **8-7** and **8-16**; **8-8** and **9-3**; **8-9**, **8-10** and **9-5**; **9-6** and **9-14**; **9-8** and **9-16**; **9-12** and **9-18**) or increases (compounds **8-3** and **8-16**; **8-11** and **9-5**; **8-14** and **9-2**; **9-7** and **9-15**; **9-9** and **9-17**, tables 8, 9) the clearing temperatures. The melting temperatures also show decreased (compounds **9-8** and **9-16**; **9-12** and **9-18**) or increased (compounds **8-3**, **8-7** and **8-16**; **8-8** and **9-3**; **8-9**–**8-11** and **9-5**; **8-14** and **9-2**; **9-6** and **9-14**; **9-7** and **9-15**; **9-9** and **9-17**; tables 8, 9) values. The cyano group is still one of the most thermally effective groups, providing the highest melting temperature among the substituted *trans*-4-*n*-pentylbicyclohexyls (compound **8-17**, table 8). As can be seen from table 9, fluorination of cyanostilbene significantly lowers the nematic thermostability, while the exchange of the cyano group and fluorine atom in this group results in the disappearance of the mesophase (compounds **9-12**, **9-13** and **9-18**).

It has been reported that moving the CF_2 group in a fluoroalkyl terminal substituent having the same quantity of the carbon and hydrogen atoms away from the rigid bicyclohexyl core, increases the clearing points and lowers the melting temperatures [34].

In contrast to the results received for biphenyls and phenylcyclohexanes, the terminal halogenation of two-ring heterocyclic derivatives of pyridin-2,5-diyl, pyrimidin-2,5-diyl and *trans*-1,3-dioxan-2,5-diyl has a more pronounced effect on their mesomorphic properties, leading in some cases to higher clearing temperatures of their mostly smectic mesophases than those of the nematic phases of the corresponding cyano derivatives (compounds **10-2**–**10-4** and **10-9**, table 10, and [22, 23]). The OCF_3 group is more efficient than $OCHF_2$ and CN groups for pyridin-2,5-diyl derivatives (compounds **10-4** and **10-3**, **10-9**) and for pyrimidin-2,5-diyl and *trans*-1,3-dioxan-2,5-diyl derivatives (only $OCHF_2$ group) [22]. Terminal substitution by F, $SCHF_2$, of OCF_2Cl groups (compounds **10-1**, **10-5**, **10-6**, and [22, 24]) does not create mesophases, nor for the phenylcyclohexanes, as was observed (table 6). Perfluoro(alkoxy)alkylation of two-ring pyridin-2,5-diyl and pyrimidin-2,5-diyl derivatives results in increasing the melting and clearing points (compounds **10-7** and **10-8**; **10-10** and **10-11**; and [22, 163]); it also reduces the number of mesophases (compounds **10-10** and **10-11**, and [22, 163]) or changes the structure of the mesophase (compounds **10-7** and **10-8**). Partial fluorination of the alkyl and alkoxy groups also increases the melting and clearing temperatures with increase in fluorine content [163–167]. The importance of the quantity of fluorine atoms and their positions in the terminal groups on the mesomorphic properties of liquid crystalline pyrimidin-2,5-diyl derivatives has been demonstrated in [168].

2.1.3. *Three- and four-ring derivatives and miscellaneous systems*

As expected, the terminal halogenation of three-ring derivatives gives a more pronounced effect on their mesomorphic properties in comparison with that observed for the one- and two-ring derivatives discussed in the previous paragraphs. It has been shown that the terminal substitution of aromatic and heteroaromatic systems by halogen or halogenated groups leads to the formation of smectic phases which exhibit high melting and in some cases high clearing temperatures, while the introduction of cyclohexane or cyclohexene rings into these systems gives rise to the nematic phase which is dominant in the corresponding cyano derivatives (tables 10–14 and [22–24, 162, 169, 170]).

As is evident from tables 11-14, the terminal halogen substitution of three-ring derivatives leads to an increase in clearing temperatures (compounds **11-1**–**11-3** and **12-16**, **13-1**–**13-3** and **14-1**, and [34, 38, 40, 189, 190]), and increasing (compounds **11-1**–**11-3** and **12-16**, **13-3** and **14-1**, and [34, 38, 40, 47, 189, 190]) or decreasing melting points (compounds **13-1**, **13-2** and **14-1**, and [38]). It is interesting to note that the order parameter, depending on the terminal substituent for compounds **11-1**–**11-3, 12-16**, **12-17**, grows as follows [42]: $F < H < Cl < Br < CN$.

The thermal data presented in tables 11 and 13 and [34, 38, 40, 45, 47, 189–195] reveal that the efficiency of the halogens introduced into the terminal position of three-ring liquid crystalline derivatives increases in the following order: $F < I < Cl < Br$. However, this order may be changed upon introducing linking groups or lateral substituents and/or replacing the molecular fragments [34, 45, 196] $F < Br < Cl$; and [47] $F < Cl < I < Br$; and [38] $F < Cl \approx Br$.

The melting temperature depends on the structure of the terminal halogen substituent in the following ways (tables 11, 13, and [34, 38, 40, 45, 47, 189–194, 197]) $F < Cl < Br < I$; and [47, 195] $Cl < F < Br$; and [34] $Cl < Br < F$; and [193] $F < Cl \approx I < Br$.

Considering the phase transition temperatures of CF_3, OCF_3, SCF_3, CHF_2, $OCHF_2$, $SCHF_2$, and the corresponding CH_3 and OCH_3 derivatives, we can derive the following statement: the clearing temperatures of trifluoromethoxy and difluoromethoxy derivatives are higher than those of the corresponding trifluoromethyl and difluoromethyl derivatives, respectively (compounds **11-5** and **11-6**, **13-5** and **13-6**, **11-4** and **11-8**, and [23, 33–35, 105, 179, 198–213]). An increase (compounds **13-16** and **14-2**) or decrease (compounds **12-14** and **12-15**) in clearing points are observed for three-ring methoxy derivatives in comparison with those of the corresponding methyl derivatives. The melting temperatures show lower (compounds **11-5** and **11-6**, **13-5** and **13-6**, and [23, 34, 35, 198–206, 210–213]) or higher [23, 201] values for trifluoromethoxy derivatives in comparison with those of the corresponding trifluoromethyl derivatives. As is evident from table 11 and the references, difluoromethoxy derivatives show lower melting temperatures than those of the corresponding difluoromethyl derivatives (compounds **11-4** and **11-8**, and [23, 33, 105, 179, 203]).

The partial and total fluorination of the methyl group (CH_3 and CHF_2, CF_3 groups) and total fluorination of the methoxy group (OCH_3 and OCF_3 groups) decreases their mesogenic efficiencies (compounds **12-15** and **11-8**, **11-6**; **13-16** and **13-6**; **12-14** and **11-5**; **14-2** and **13-5**; tables 11-14, and [22, 23, 34, 40, 49, 156, 169, 177, 182, 192, 199, 214–217]), while the partial fluorination of the latter group (OCH_3 and $OCHF_2$ groups) increases (compounds **12-14** and **11-4**) or decreases (compounds **14-2** and **13-4**, tables 13, 14, and [22, 23, 40, 182, 215]) its efficiency. There are some exceptions from these rules: increasing the length of the alkoxy group and the replacement of one of the molecular fragments in the core lead to higher clearing temperatures of three-ring CF_3 and OCF_3 derivatives compared with those of the corresponding CH_3 and OCH_3 derivatives, respectively [49, 169]. As can be seen from tables 11–13 and the references, trifluoromethyl and difluoromethyl drivatives exhibit higher (compounds **11-6**, **11-8** and **12-15**, **13-6** and **13-16**, and [23, 49, 192, 216, 218]) or lower [23, 33, 177, 182, 217] melting temperatures than the corresponding methyl derivatives.

The thermal data collated in tables 11–14 and the references shows that difluoromethoxy and trifluoromethoxy derivatives show lower (compounds **11-4**, **11-5** and **12-14**; **13-4**, **13-5** and **14-2**; and [22, 23, 34, 40, 169, 182, 199, 215, 219]) or higher [156, 179, 212, 215] melting points than the corresponding methoxy derivatives. The difluoromethoxy group is more efficient than the trifluoromethoxy group (compounds **10-12** and **10-13**, **11-4** and **11-5**, **13-4** and **13-5**, and [22, 23, 36, 179, 203, 212, 215, 220–224]), while the replacement of one of the molecular fragments and the introduction of linking groups lead to the opposite order [23, 199], also observed for two-ring pyridin-2,5-diyl derivatives presented in table 10. From tables 10, 11, 13 and the references, it can be seen that difluoromethoxy derivatives show higher (compounds **10-12** and **10-13**, **11-4** and **11-5**, **13-4** and **13-5**, [22, 23, 203]) or lower [23, 179, 203, 212, 215, 225, 226] melting temperatures than the corresponding trifluoromethoxy derivatives. Replacement of oxygen by sulphur in the OCF_3 and $OCHF_2$ groups to give SCF_3 and $SCHF_2$ groups respectively, significantly lowers their mesogenic efficiency (compounds **10-12** and **10-14**, **11-4** and **11-7**, **11-5** and **11-9**, **13-5** and **13-7**, tables 10, 11, 13 and [22]). The melting points show a decrease for $SCHF_2$ derivatives (compounds **10-12** and **10-14**, **11-4** and **11-7**) and an increase for SCF_3 derivatives (compounds **11-5** and **11-9**, **13-5** and **13-7**). A similar decrease in the thermal efficiency caused by replacing the carbon atom by a sulphur atom in other terminal groups is shown in table 11 for compounds **11-10** and **11-14**, **11-11** and **11-16**.

As discussed above, terminal chloro substitution is more efficient than fluoro substitution, however, the replacement of fluorine by chlorine in the trifluoromethoxy group to give the difluorochloromethoxy group lowers the thermal efficiency (compounds **10-13** and **10-15**, **13-5** and **13-9**, [22, 24, 227]). The melting temperatures of difluorochloromethoxy derivatives exhibit higher (compounds **10-13** and **10-15**, **13-5** and **13-9**, tables 10, 13, and [22, 24, 227]) or lower [22, 24] values in comparison with those of the corresponding trifluoromethoxy derivatives. A similar decrease in thermal efficiency has been reported for other chlorofluoro-substituted groups (compounds **11-11** and **12-11**, tables 11, 12).

A comparison of the phase transition temperatures of compounds **12-1**–**12-5** and **12-13**; **13-11** and **14-3**; **14-4** and **14-5**; **14-6**, **14-7** and **14-8** reveals an influence of the fluorination content and positions of the fluorine atoms in polyfluorinated groups on their efficiency, which decreases with the increase in fluorine content (see also [51]). Again, it is difficult to explain these results in terms of the Mayer–Saupe theory, since increasing the fluorine content of the terminal groups results in an increase in their anisotropy of polarizability (see the additive scheme of its calculation proposed in [228–230] and table 1) which in turn, according to Mayer and Saupe [122], should enhance the stability of the mesophase. The melting temperatures of these derivatives show a decrease (compounds **14-4** and **14-5**, **14-6** and **14-8**, and [51]) or increase (compounds **12-1**–**12-5** and **12-13**, **14-7** and **14-8**, tables 12, 14), with increase of fluorine content.

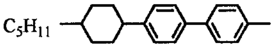
It is useful to express the effect of halogenation of the terminal substituents on the mesomorphic properties of LCs in the order of increasing clearing temperatures

(T_{clp}), nematic range ΔT, melting temperatures (T_{m}), and smectic thermostabilities (T_{s}), depending on the structure of the terminal substituent Z in the system (I) (tables 11, 12), and system (II) (tables 10, 11):

As is evident from these orders, halogen-substituted alkenyl groups (even those containing two different halogen atoms) show enhanced thermal efficiency in comparison with other groups. Increasing the length of the polyfluorinated groups leads to increasing smectic thermostability and decreasing nematic range. Sulphur-containing fluorinated groups usually exhibit decreased values of thermal efficiency. The cyano group is still one of the most thermally efficient groups providing a wide nematic range with moderate melting point, lower than that of some halogenated and hydrogenated groups exhibiting lower polarity [123]. These findings in the melting temperatures do not support the suggestion that an increase in polarity of the terminal substituents should increase the melting temperature [124].

As can be seen from tables 13 and 14, partial fluorination of the propyl group results in the disappearance of the smectic phase and the creation of only the nematic phase with a lower clearing point (compounds **14-9** and **13-1**). Similar results have been reported for other three-ring liquid crystalline derivatives containing two non-symmetrical halogenated terminal groups [202, 208, 231].

It has been shown that the introduction of the same halogen in both terminal positions of three-ring *p*-phenylene dibenzoates results in the formation of a



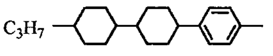
(I) *System (I)*

Tclp ⇨ Z: $CF_2CN < H < SCF_3 < SOCHF_2 < CF_2CH_2CF_3 < SCHF_2 < COCF_2Cl < CF_3 < COCF_3 < OCF_3 < F < COCHF_2 < CH_2CHFCH_3 < CHF_2 < OCH_3 < OCHF_2 < C_3H_7 < COOCH_2CF_3 < OCF_2CH{=}CH_2 < CH_3 < OCF_2CHFCF_3 < Cl < COCF_2CH_3 < Br < OCH_2CH{=}CF_2 < OCH_2CHF_2 < CN < CH{=}CF_2$

ΔT ⇨ Z: $CF_3 < OCH_2CH{=}CF_2 < COOCH_2CF_3 < SOCHF_2 < C_3H_7 < CH_2CHFCH_3 < OCH_2CHF_2 < H < SCHF_2 < OCF_3 < COCF_2CH_3 < Br < CHF_2 < OCHF_2 < CH{=}CF_2 < Cl < CH_3 < F < COCF_3 < COCF_2Cl < COCHF_2 < OCH_3 < CN$

Tm ⇨ Z: $C_3H_7 < OCF_3 = CH_2CHFCH_3 < COCF_2CH_3 = COCF_2Cl < OCH_2CH{=}CF_2 < SCHF_2 < CH{=}CF_2 < H < CF_2CN < SCF_3 < OCHF_2 < COCF_3 < OCH_3 = COCHF_2 < CF_2CH_2CF_3 < COOCH_2CF_3 < OCH_2CHF_2 < F < CN < CH_3 < SOCHF_2 < SOOCHF_2 < CHF_2 < SOCF_3 = CF_3 < Cl < CHFCF_2CH_3 = CF_2CF_2CH_3 < CH_2CF_2CH_3 < Br < OCF_2CHFCF_3 < OCF_2CH{=}CH_2$

Ts ⇨ Z: $SCF_3 < H < SCHF_2 < CF_2CH_2CF_3 < OCHF_2 < CH_3 < OCF_3 < CH_2CHFCH_3 < C_3H_7 < COOCH_2CF_3 < COCF_2CH_3 < OCF_2CHFCF_3 < CH{=}CF_2 < OCH_2CHF_2 < OCH_2CH{=}CF_2$



(II) *System (II)*

Tclp ⇨ Z: $H < SCF_3 < OCF_2Cl < CH_2OCH_2CF_2CHF_2 < OCF_3 < F < CH_2OCH_2CF_3 < OCHF_2 < N(CH_3)CF_3 < C_3H_7 < CH_3 < N(CH_3)CH_3 < I < Cl < COCF_2CH_3 < OCH_3 < CH{=}CF_2 < CN < CF{=}CHCl$

ΔT ⇨ Z: $H < I < OCF_2Cl < SCF_3 < F < CH_3 < OCH_3 < OCF_3 < OCHF_2 < COCF_2CH_3 < Cl < CH{=}CF_2 < CN < CF{=}CHCl$

Tm ⇨ Z: $N(CH_3)CF_3 < C_3H_7 < CH_2OCH_2CF_3 < CH_2OCH_2CF_2CHF_2 < OCF_3 < OCHF_2 < SCF_3 = CH{=}CF_2 < F < N(CH_3)CH_3 < CH_3 < Cl < CN < OCH_3 < OCF_2Cl < COCF_2CH_3 < CF{=}CHCl < I < SF_5 < CF_3 < C_2F_4CH_3$

Ts ⇨ Z: $OCF_3 < OCHF_2 < Cl < CN < CH{=}CF_2 < H < F < CH_3 < OCH_3 < I < CH_2OCH_2CF_2CHF_2 < CH_2OCH_2CF_3 < N(CH_3)CF_3 < C_3H_7 < N(CH_3)CH_3$

Scheme. Mesophase properties of system I and system II compounds.

nematic phase that exhibits high melting and clearing temperatures, with the following dependences on the terminal substituents [124, 232]: $T_m, T_{clp} \rightarrow H < F < Cl < Br < CN$. These results have been explained in terms of the principal influence of the size of the terminal substituents and their polarity and polarizability on phase transition temperatures.

Symmetrical perfluoroalkoxylation in both terminal positions creates mostly smectic phases in comparison with the non-mesomorphic or mostly nematic character of mesophases observed in the corresponding di-perfluoroalkylated *p*-phenylene dibenzoates [94, 114]. Decreasing the fluorination content of the terminal substituents in these compounds enhances the clearing and melting temperatures (for most members) [94, 114, 233].

It has been demonstrated that di-halogen substitution in both terminal positions of α,α′-bis-(4-substituted methylphenylimino)-*p*-xylene gives a nematic phase showing high melting and clearing temperatures, with the following dependences on the terminal substituents [115]:

$$T_m \rightarrow F < H < Cl < CF_3 < CH_3 < Br < CN < I$$

$$T_{clp} \rightarrow F < I < CH_3 < Cl \approx Br < CN.$$

Interestingly, the introduction of the fluorine atom creates the nematic phase and lowers the melting point, while replacement of the methyl group by trifluoromethyl decreases the melting point and leads to the disappearance of the mesophase [115]. The decreased efficiency of the CF_3 group in comparison with the CH_3 group has been explained in terms of the increased size of the former, which broadens the molecule, thereby reducing the effective lateral attractive forces between molecules in the nematic phase. Another reason is the dipole properties of the CF_3 group, which produces instantaneous repulsions between neighbouring molecules. It has been proposed that these repulsions will be less significant in the case of the less polar CH_3 group [115].

Let us discuss in detail the effect of halogenation on the alkenyl group which is clearly shown in table 14 for compounds **14-10**–**14-18**. Halogenation of the alkenyl group increases melting and clearing temperatures (compounds **14-10** and **14-12**; **14-13** and **14-14**; **14-15** and **14-16**, and [36, 187]). The introduction of two halogen atoms (the same or different) in both terminal groups (one of them is the alkenyl) results in the formation of only the nematic phase with high melting and clearing points (compounds **14-13**, **14-15**, **14-17**, **14-18**, and [142]). Bromine has been found to be more efficient than chlorine in the halogenation of alkenyl groups (compounds **14-17** and **14-18**). Similar results, demonstrating the effect of terminal halogenation of four-ring liquid crystalline derivatives on their mesomorphic properties, have been presented in [208, 222, 234–242].

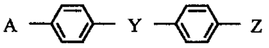
Lastly, there have been some reports showing the effects of perfluoroalkylation on the mesomorphic behaviour of liquid crystalline carbohydrates [242], discotic liquid crystals [243], laterally long branched mesogens [244], swallow liquid crystals [245–247].

2.2. *Linking substitution*

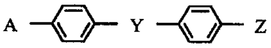
It has been demonstrated that the introduction of the following fluorinated linking groups into the molecular core of two-ring 1,4-phenylene derivatives does not produce a mesophase [32, 248]: CF_2CHF, CF_2CF_2, OCF_2, SCF_2.

The *trans*-α, β-difluorostilbene group shows a remarkable ability to enhance mesomorphism (compounds **15-1** and **15-3**–**15-6**; **16-6** and **16-7**, **16-9**–**16-13**; tables 15, 16, and [258]) which, however, can be less thermostable than that of the corresponding hydrogen derivative (compounds **16-6** and **16-8**, table 16). Similarly, the incorporation of the CF=CF unit into the linking groups increases the nematic thermostability (compounds **15-2** and **15-4**, **15-13** and **15-16**, **16-1** and **16-3**–**16-5**, tables 15, 16, and [28, 265, 266]) which can be higher (compounds **15-2** and **15-3**, **15-13** and **15-14**, table 15) or lower (compounds **16-1** and **16-2**, and [250]) than those of the corresponding hydrogenated derivatives. These results might be correlated with the fact that fluorination of the *trans*-stilbene group causes a small deformation of the π-electron distribution which raises the vacant orbitals and increases the effects of interaction of the π-electrons in this group with the π-electron system of a benzene ring [267].

As seen from table 15, increasing the quantity of the CF=CF linking units leads to a pronounced odd–even effect in the clearing temperatures (compounds **15-7**–**15-11**), opposite behaviour to that of the corresponding di-methyl derivatives [29]. The observed decrease in the melting and clearing temperatures for the 1,4-diphenylperfluoro-1,3-butadiene derivative **15-7** in comparison with those of the corresponding hydrogen derivative **15-12** has been explained in terms of the disruption of the planarity of the *transoid* system (compound **15-12**) and its transformation into the non-planar *cisoid* system (compound **15-7**) [29]. This is accompanied by a shortening of the C=C bond length. It might be useful to consider the structure of these compounds for a possible explanation of the results. Firstly, α,β-difluorostilbene is non-planar and the torsional angle between the benzene rings relative to the C=C bond is equal to 25–26° [29, 268]. Secondly, α,ω-diarylperfluoropolyenes $Ar(CF{=}CF)_nAR$, where $n = 2$–4, show all-*trans* configurations of the fluorine atoms and exist in twisted non-planar *cisoid* conformations with rotation angles ranging from 0 to 23°. Torsional angles of the double bond planes relative to each other are from 47°

Table 15. Mesomorphic properties of liquid crystals: 

Compound	A	Y	Z	Phase transitions/°C	Ref.
15-1	CH_3	CF=CF	CN	Cr 126.6 X 167.5 I	[249]
15-2	CH_3	CF=CFCOO	CN	Cr 118 N 137 I	[250]
15-3	CH_3	CH=CHCOO	CN	Cr 127 N 127.5 I	[250]
15-4	CH_3	COO	CN	N 63.3 I	[251]
15-5	CH_3	C≡C	CN	Cr 160 I	[252]
15-6	CH_3	—	CN	Cr 109 I	[253]
15-7	CH_3O	$(CF{=}CF)_2$	OCH_3	Cr 84 Sm 95 N 196 I	[29]
15-8	CH_3O	$(CF{=}CF)_3$	OCH_3	Cr 101 N 204 I	[29]
15-9	CH_3O	$(CF{=}CF)_4$	OCH_3	Cr 95 Sm 102 N 195 I	[29]
15-10	CH_3O	$(CF{=}CF)_5$	OCH_3	Cr 103 N 207 I	[29, 254]
15-11	CH_3O	$(CF{=}CF)_6$	OCH_3	Cr 82 N 176 I	[29]
15-12	CH_3O	$(CH{=}CH)_2$	OCH_3	Cr 225 N 238 I	[29]
15-13	CH_3O	CF=CFCOO	OCH_3	Cr 129 N 158 I	[250]
15-14	CH_3O	CH=CHCOO	OCH_3	Cr 118 N 137 I	[250]
15-15	CH_3O	CH=CH	OCH_3	Cr 216 N (176) I	[255]
15-16	CH_3O	COO	OCH_3	Cr 125 I	[256]
15-17	CF_3	CBr=CH	OCH_3	Cr 102 I	[257]
15-18	CF_3	CBr=CBr	OCH_3	Cr 198 I	[257]

Table 16. Physico-chemical properties of liquid crystals: 

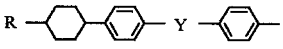
Compound	A	Y	Z	Phase transitions/°C	$\varepsilon_{\perp}$[a]	$\Delta\varepsilon$[a]	Ref.
16-1	C_3H_7	C≡CCF=CFC≡C	C_3H_7	Cr 90 N 144.1 I			[259]
16-2	C_3H_7	C≡CCH=CHC≡C	C_3H_7	Cr 95.3 N 162.3 I			[260]
16-3	C_3H_7	C≡C	C_3H_7	Cr 73 I			[196]
16-4	C_3H_7	C≡CC≡C	C_3H_7	Cr 107.5 N 131.9 I			[261]
16-5	C_3H_7	—	C_3H_7	Cr 61.2 I			[139]
16-6	CH_3O	CF=CF	C_5H_{11}	Cr 39.8 X 90.4 I			[249]
16-7	CH_3O	CCl=CH	C_5H_{11}	Cr 35.9 N 51.4 I	4.09	− 0.390	[262]
16-8	CH_3O	CH=CH	C_5H_{11}	Cr 118 SmB (109.5) N 124.5 I	2.83	+ 0.138	[262]
16-9	CH_3O	COO	C_5H_{11}	Cr 28.9 N 41.5 I	5.61	+ 0.073	[262]
16-10	CH_3O	N=CH	C_5H_{11}	Cr 48.6 N 63.7 I	4.27	− 0.335	[262]
16-11	CH_3O	CH=N	C_5H_{11}	Cr 40.3 N 62.9 I	4.67	− 0.352	[262]
16-12	CH_3O	N=N	C_5H_{11}	Cr 39.4 N 65.4 I	3.20	+ 0.209	[262]
16-13	CH_3O	C≡C	C_5H_{11}	Cr 43 N 55 I	3.47	+ 0.140	[263]
16-14	C_2H_5O	CCl=N	C_5H_{11}	Cr 47 N 48 I			[264]
16-15	C_2H_5O	CH=N	C_5H_{11}	Cr 63 N 90 I			[264]

[a] $\tau = 0.97$.

to 49° [29, 269, 270]. It has been found for compounds with $n = 5, 6$, that their torsional angles are similar to those of compounds with $n = 2$–4, while their structures comprise the *cisoid* and *transoid* parts [29].

The data collated in tables 15, 16 reveal that α,β-bromination and α-chlorination of *trans*-stilbene results in the disappearance of the mesophase and decrease of the melting points (compounds **15-15** and **15-17**, **15-18**) or decrease of the melting and clearing points (compounds **16-7** and **16-8**). It has been explained in terms of disruption of the *trans*-stilbene planarity [255]. In comparison with other linking groups, the CCl=CH group shows lower (except compound **16-9**) nematic thermostability (compounds **16-7** and **16-6**, **16-8**, **16-10**–**16-13**). A similar decrease in the melting and clearing temperatures has been observed for chlorinated Schiffs base (compounds **16-14** and **16-15**).

As expected, the halogenation of linking groups introduced into the molecular core of three-ring derivatives gives a more pronounced effect on their phase transition temperatures, consistent with the results seen for two-ring systems (compounds **17-1**–**17-7**, **11-5**; **17-8**–**17-12**, **11-1**; **17-13** and **17-14**, table 17). The introduction of the difluoromethoxy group lowers the clearing temperatures (compounds **17-1**, **17-2** and **11-5**; **17-8** and **11-1**; **17-13** and **17-14**), and increases (compounds **17-2** and **11-5**) or decreases (compounds **17-8** and **11-1**, **17-13** and **17-14**) the melting temperatures in comparison with those of the

Table 17. Physico-chemical properties of liquid crystals: , R = C_5H_{11}

Compound	Y	Z	Phase transitions/°C	$\Delta\varepsilon^{a}$	Δn^{a}	$v^{a}/mm^2\ s^{-1}$	Ref.
17-1	OCF_2	OCF_3	Cr 43 SmB 116 I	4.5	0.107	10	[32]
17-2	CF_2O	OCF_3	Cr 68.3 SmB 80.5 N 90.2 I				[271]
17-3	CF=CF	OCF_3	Cr 78 Sm_1 122 Sm_2 190 N ? I				[272]
17-4	CH=CH	OCF_3	Cr 72 Sm 168 N 224 I		0.180^{b}	54^{b}	[199]
17-5	C≡C	OCF_3	Cr 50 SmB 134 SmA 167 N 189.9 I	9.9^{b}	0.219^{b}	18^{b}	[23]
17-6	CH_2CH_2	OCF_3	Cr 47 SmB 68 N 73.7 I	7.2^{b}	0.104^{b}	16^{b}	[23]
17-7	COO	OCF_3	Cr 106 SmB (84) SmA 131 N 167.9 I I	15.3^{b}	0.134^{b}	35^{b}	[23]
11-5	—	OCF_3	Cr 43 SmB 128 N 147.4 I	8.9^{b}	0.140^{b}	16^{b}	[23]
17-8	OCF_2	F	Cr 50 SmB 58 N 106 I	2.8	0.095	15	[32]
17-9	CF_2CF_2	F	Cr 69 I	3.5	0.092		[248]
17-10	CH_2CH_2	F	Cr 57 N 79 I				[191]
17-11	C≡C	F	Cr 85.8 SmG 91.8 N 187.5 I I		0.230	24	[273, 274]
17-12	COO	F	Cr_2 82 Cr_1 93 N 156 I	3.9^{c}			[40]
11-1	—	F	Cr 94.4 N 152.9 I	4.6^{f}	0.098^{h}	24.7^{g}	[14, 30, 171]
17-13^{d}	CF_2O	OCF_3	Cr 58.2 SmB 70.9 N 83.1 I	9.7^{e}	0.109	11	[32, 271]
17-14^{d}	—	OCF_3	Cr 90 SmB 129 N 151.4 I	8.9^{b}	0.166^{b}	14^{b}	[23]

[a,b] Extrapolated from 10 wt % solution in ZLI-4792 and ZLI-1132, respectively, measured at 20°C.

[c] $\tau = 0.93$.

[d] $R = C_3H_7$.

[e] Extrapolated from 20 wt % solution in the liquid crystalline mixture at 25°C.

[f,g] Extrapolated from 20 wt % solution in the mixture of 2,4-difluoroderivatives, measured at 25 and 20°C, respectively.

[h] $\tau = 0.95$.

corresponding derivatives without linking groups. The influence on mesomorphic properties of the position of the difluoromethoxy group in the molecular core of LCs is clearly shown in table 17 by comparison of the thermal data of compounds **17-1** and **17-2**. So far, pointing the oxygen of the difluoromethoxy group toward the 4-trifluoromethoxyphenyl fragment (compound **17-2**) increases the melting and lowers the clearing temperature, and does not change the number of mesophases compared with the parent compound **11-5**. Pointing that oxygen in the opposite direction (compound **17-1**) results in the disappearance of the nematic phase, and decreasing or increasing, respectively, the clearing point in comparison with those of the parent compound and compound **17-2**. As was observed for two-ring derivatives, *trans*-α,β-difluorostilbene shows increased efficiency in comparison with that of the corresponding derivatives without linking groups or having OCF_2, C≡C, CH_2CH_2 and COO linkages (compounds **17-3** and **11-5**, **17-1**, **17-2**, **17-5**–**17-7**), and increased melting temperature compared with that of the corresponding *trans*-stilbene derivative **17-4**. Interestingly, full fluorination of the ethylene group leads to the disappearance of the mesophase (compounds **17-9** and **17-10**). Similar results have been reported for four-ring derivatives [275].

The presented results reveal that the terminal and linking halogenation of achiral liquid crystals may increase or decrease the thermal stability of the mesophases compared with that of corresponding hydrogenated derivatives. The importance of the structure of liquid crystals, their substituents, and their halogen content and its distribution is also shown. These findings are not consistent with the theory of Maier and Saupe which states that the stability of the mesophase is proportional to the anisotropy of polarizability of the molecules forming the mesophase [122]. In such cases, halogenated LCs, having increased values of the anisotropy of polarizability than those of corresponding hydrogenated liquid crystalline derivatives (see table 1), should consequently exhibit increased values of the nematic–isotropic liquid transition temperatures in comparison with those of the hydrogenated LCs. However, some of the results presented here and in [21, 34, 39, 51, 59, 60, 276] do not support this suggestion.

It seems that there is no direct correlation between the electronic structure of the halogenated terminal and linking groups (characterized by Hammet substituent constants and resonance and field parameters [18, 277, 278]), and the mesomorphic properties of LCs incorporating them. However, the electronic structure of halogenated groups [7, 17–20, 265, 279–290] plays a very important role in the intra- and inter-molecular interactions which affect the packing of the molecules which predominantly influences mesophase thermostability [291–294]. 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 [292]. Other aspects such as molecular association [295] or dipole–dipole attraction in polar liquid crystalline derivatives, which can influence the packing of the molecules, also affect the stability of the mesophases [292]. Particularly in perfluoroalkylated derivatives, the perfluoroalkyl group, which is more rigid and linear than the corresponding alkyl group [65, 75–77, 89, 102, 161, 293] promotes microphase segregation [67, 87, 102, 245, 296] and strong electrostatic interactions, such as fluorophobic [65–68, 74–78, 87, 102, 245, 296] and fluorophilic [49, 74] interactions around the perfluoroalkyl groups, that can be responsible for the pronounced layer arrangements of molecules and phase formation.

X-ray diffraction (XRD) of the liquid crystals is a useful method for studying the effects of the association of liquid crystalline molecules on the structure of their phases and consequently on the properties of LCs formed by these molecules [72, 161, 297–302]. 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 having a 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 a molecular length, is about 1.2–1.5 [297, 298, 300, 301]. 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 polar LCs and characterizes, in particular, the degree of overlap of the molecular cores in dimer formation. Further XRD investigations of the nematic phase of polar LCs revealed in some cases the simultaneous existence of two fluctuation layer structures with incommensurate periods d_1 and d_2, where $d_1 < L$ and $L < d_2 < 2L$ [297, 299, 300, 301].

It has been reported that the XRD pattern of two-ring 2,5-disubstituted pyridine cyano derivatives shows two incommensurate density waves: monomeric with period d_1 (period d_1 is related to the fluctuation layer structure formed by separate molecules) and dimeric with period d_2 [297, 300, 303]. The replacement of the cyano group by trifluoromethoxy (compounds **10-4** and **10-9**, table 10) results in the appearance of the smectic B and smectic A phases [161]. XRD studies of compound **10-4** reveal a remarkable change in the structure of its mesophases. Only one density wave was observed, with an interlayer spacing greater than the molecular length: $d/L \approx 1.05$–1.10. Depending on the temperature, this corresponds to the creation of a partly bilayer A_d phase in which the molecules are shifted relative to one another in an antiparallel configuration [161]. Similar results have been presented showing the formation of the monolayer smectic [39, 46, 76–78, 91, 93, 161, 245–247, 304, 305], partly bilayer smectic [49, 65, 67, 68, 72, 74, 76, 77, 90, 102, 161, 246, 247, 296], bilayer smectic [65], and bilayer-like smectic phases with the ratio $d/L \leqslant 1$ [164] in LCs containing halogen(s) substituted terminally and linking groups.

3. Static dielectric properties

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, ($\varepsilon_\parallel$ and $\varepsilon_\perp$ are, respectively, dielectric constants parallel and perpendicular to the nematic director **n**) and the molecular structure of LCs is described by the theory of Maier and Meier [306]:

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

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 (as well as optical and elastic) properties of LCs with different nematic–isotropic phase transition temperatures $T_{\text{N-I}}$ can only be made at a constant reduced temperature $\tau = T_{\text{meas}}/T_{\text{N-I}}$ [6].

Tables 6, 8, 10–13, 16 and 17 present data on the dielectric properties of liquid crystalline compounds measured at a constant reduced temperature and extrapolated from the liquid crystalline mixtures at 20 or 25°C. According to [6], the extrapolations are not meaningful; however these estimations are the only way to obtain a rough definition of the dielectric (as well as optical and elastic) properties of non-mesomorphic compounds, smectic LCs and LCs with a narrow nematic range. From these tables, it follows that for the definite molecular structure of LCs, their dielectric anisotropy decreases approximately in the same sequence as the values of dipole moments for the terminal groups: SO_2CF_3, SO_2CHF_2, CN, $SOCHF_2$, $SOCF_3$, SF_5, CF_3, SCF_3, $SCHF_2$, $OCHF_2$, OCF_3, Cl, Br, F, I, OCH_3, CH_3 diminish: 4.32, 4.08, 4.05, 3.93, 3.88, 3.44, 2.54, 2.50, 2.48, 2.46, 2.36, 1.59, 1.57, 1.47, 1.40, 1.28, 0.37 D [18, 22, 123, 307]. Taking into consideration the angles β of the dipole moments could provide a more accurate analysis of the dielectric properties of the LCs presented [18, 123, 307].

As is evident from table 16, α-chlorination of *trans*-stilbene introduces an extra dipole moment that contributes much more to $\varepsilon_\perp$ than to $\varepsilon_\parallel$, leading to a negative value of the diectric anisotropy which is highest (in absolute value) among the compounds under consideration (compounds **16-7** and **16-8**–**16-13**). Similar results have been found for the CF_2CF_2 linking group (compounds **17-9** and **11-1**, table 17). These facts are employed for the design of LCs exhibiting a high negative dielectric anisotropy for active matrix display applications [308].

The introduction of the difluoromethoxy linking group into the molecular core of LCs also significantly affects their dielectric anisotropy, lowering (compounds **17-1** and **11-5**, **17-8** and **11-1**) or increasing (compounds **17-13** and **17-14**, table 17) its value. These results show the importance of the position of the difluoromethoxy linking group and, consequently, the direction of its dipole moment in the molecular core, leading to a decrease or increase of the total dipole moment in these cases.

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 [309–312], but antiparallel association predominates and reduces the effective dipole moment [295]:

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

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

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 presented in [276, 313] reveal that the replacement of a cyano group by a chloro group in two-ring *trans*-1,4-cyclohexylene derivatives (compounds **6-16**, **7-1**, table 6, 7) results in increasing the factor g from 0.590 to 1.20 which corresponds to the change of character from antiparallel to parallel association.

4. Optical properties

The phenomenological relation between refractive index and electric polarization is defined as [314, 315]:

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

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 is the extraordinary refractive indices. From equation (4) and the previous section, it follows that compounds which have a large induced polarizability of their highly conjugated π-electron system (for example, cyano derivatives) exhibit an optical anisotropy $\Delta n = n_e - n_o$ which is much larger than that of the corresponding halogen(s)-substituted derivatives, see tables 6, 8, 10–13 and [4, 22, 23]. Increasing the fluorination content in the terminal groups ($OCH_3 \rightarrow OCHF_2 \rightarrow OCF_3$) further decreases the optical anisotropy (compounds **6-6** and **6-2**, **6-3**; **10-3** and **10-4**; **10-12** and **10-13**; **11-4** and **11-5**; **13-4** and **13-5**, tables 6, 10, 11, 13, and [22, 23]). The growth in the Δn values for F-, Cl-, and Br-substituted derivatives can be correlated with the corresponding increase of their anisotropy of polarizability and decrease of their electronegativity (compounds **11-1**–**11-3**, **13-1** and **13-2**, tables 1, 11, 13) [14, 41, 316]: $\Delta n \rightarrow \text{F} < \text{Cl} < \text{Br}$.

A similar decrease in optical anisotropy can be observed for compounds incorporating fluorinated linking groups (compounds **17-1** and **17-4**–**17-7**, **11-5**; **17-8**, **17-9** and **17-11**, **11-1**; **17-13** and **17-14**, table 17). These effects can be explained in terms of a reduction in the effective conjugation of the π-electron system resulting in a shorter resonance wavelength of the UV absorption spectrum for terminally- and linking halogen(s)-substituted liquid crystalline derivatives than for the corresponding cyano derivatives and compounds without linking groups or having hydrogenated groups [267, 316–319].

5. Viscosity

It has been shown that nematic liquid crystalline materials for display applications should have a low viscosity to give acceptable response times for LCDs [6, 320]. According to the results on the kinematic viscosity v presented in tables 6, 8, 10–13 and 17, terminally- and linking halogen(s)-substituted derivatives exhibit lower values than those of the corresponding cyano derivatives and compounds without linking groups or having hydrogenated linking groups (compounds **6-1**–**6-5**, **6-7**–**6-9**, **6-14** and **6-16**; **8-2**, **8-3**, **8-8**, **8-13** and **8-17**; **10-3** and **10-9**; **11-1**, **11-4**–**11-6**, **11-9**–**11-13**, **12-3**, **12-12** and **12-17**; **13-1**, **13-2**, **13-4**–**13-7**, **13-10** and **13-17**; **17-1** and **17-4**–**17-7**, **11-5**; **17-8** and **17-11**, **11-1**; **17-13** and **17-14**, and [22, 23]; except compounds **12-2**, **12-11**), respectively. These results can be explained in terms of the different tendency for association [321] expressed by the correlation coefficient g of these compounds (see § 3); and the predominant role of the dimers and, possibly, the monomers in defining the LC properties for the cyano derivatives and compounds having short halogen-substituted terminal substituents, respectively (considering data on the correlation factor g in § 3 and on the XRD data [161, 276, 300, 322]).

As can be seen from tables 6, 11 and 12, replacement of the hydrogen atoms by fluorine in the OCH_3 group decreases the viscosity with increasing fluorine content (compounds **6-6** and **6-2**, **6-3**; **12-14** and **11-4**, **11-5**), while the partial fluorination of the C_3H_7 group and total fluorination of the CH_3 group results in an increase of viscosity (compounds **12-13** and **12-2**, **12-3**; **13-16** and **13-6**, and [33]). Interestingly, total fluorination of the alkyl groups gives a lower viscosity than that of the corresponding partly fluorinated groups containing the same quantity of carbon atoms [33]. It is important to note that in most cases the OCF_3 terminal substitution results in a lower viscosity than the corresponding $OCHF_2$ substitution (compounds **6-2** and **6-3**, **11-4** and **11-5**, **13-4** and **13-5**, tables 6, 11, 13, and [22, 23]). Also, we can note the positive role of the oxygen atom in decreasing the viscosity of the OCF_3 derivatives compared with that of the corresponding CF_3 derivatives (compounds **6-3** and **6-4**, **11-5** and **11-6**, **13-5** and **13-6**, and [23]). Moreover, the replacement of fluorine by chlorine in the $COCF_3$ group to obtain the $COCF_2Cl$ group increases the viscosity (compounds **11-11** and **12-11**, tables 11, 12).

6. Molecular packing

It has been shown that LC molecular packing plays a very important role in the creation of mesophases [291, 293] and defines their optical properties [314]. The molecular packing coefficient is expressed in [323] as:

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

where N_A is the Avogadro number, ρ is the density, M is the molecular weight, 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.

As is evident from table 10, the replacement of the CN group by F, $OCHF_2$ or $SCHF_2$ groups changes the molecular packing coefficient in the following order (compounds **10-1**, **10-3**, **10-5** and **10-9**): $k_p \rightarrow SCHF_2 < OCHF_2 < CN < F$. A decrease of the fluorine content in the terminal groups ($OCF_3 \rightarrow OCHF_2$) results in an increase in the molecular packing [324]. Similar results revealing an enhanced molecular packing of terminally halogen-substituted three-ring derivatives, in comparison with that of the corresponding cyano derivative, are shown in tables 11 and 12 for compounds **11-1**–**11-3** and **12-17**: $k_p \rightarrow CN < Br < F < Cl$.

7. Conclusion

Systematic studies on the effect of terminal- and linking-group halogenation on the physico-chemical properties of achiral liquid crystals have been performed; with attempts to correlate the molecular level parameters with observed properties. The information presented here may lead to a better understanding of the nature of liquid crystals.

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