Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 01 Mar 2010

To cite this article: Vladimir F. Petrov (2010): Halogenation in Achiral Calamitic Liquid Crystals. II Terminal and Linking Substitutions, Molecular Crystals and Liquid Crystals, 517:1, 27-42

To link to this article: http://dx.doi.org/10.1080/15421400903507763

Mol. Cryst. Liq. Cryst., Vol. 517: pp. 27–42, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903507763

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Halogenation in Achiral Calamitic Liquid Crystals. II 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 existent theories; a comparison is made with the corresponding hydrogenated and other well-known groups.

Keywords Halogen; liquid crystals; physico-chemical properties

1. Introduction

In continuation of our study of the structure–property relationships in halogen containing liquid crystals (see for example, the previous publication [1]), we present here some new details of the effect of the halogenation of achiral calamitic liquid crystals on the appearance of the mesophases and their physico-chemical properties. When possible, the properties of the halogenated liquid crystals will be compared with those of the corresponding hydrogen containing derivatives and other well-known liquid crystals.

2. Mesomorphic Properties

2.1. *Terminal Substitution*

The phase transition temperatures of the halogenated derivatives and reference compounds are presented in Tables 1–6, where Cr, Sm, SmG, SmH, SmB, SmA, N, and I denote the crystalline, smectic, smectic G, H, B, A, nematic, and isotropic phases, respectively. X is the unknown mesophase. Values given in parentheses refer to monotropic phase transitions.

It is evident from Table 1 that the pefluoroalkoxylation of two-ring 2,5-disubstituted pyrimidine derivatives results in the formation of the smectic A phase with the significantly higher melting (crystal-smectic or crystal-nematic phase transition temperatures) and clearing points (nematic-isotropic or smectic-isotropic liquid phase transition temperatures) in comparison with those of the corresponding derivatives having the polyfluorinated terminal groups with the same number of carbon atoms (compounds **1-1–1-5**).

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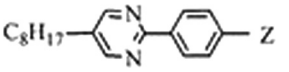
Table 1. Mesomorphic properties of liquid crystal:



No.	Z	Phase transitions, °C	Ref.
1-1	OC_9F_{19}	Cr 65.1 SmA 115.1 I	[2]
1-2	$OC_3H_6OCH_2C_5F_{11}$	I 80 SmA -21 Cr	[3]
1-3	$OCH_2C_2F_4OC_6F_{13}$	I 88 SmA 52 SmC 15 Cr	[4]
1-4	$OC_3H_6OCH_2CF_2OC_2F_4OC_2F_5$	I 84 SmA -23 Cr	[3]
1-5	$OC_5H_{10}OCH_2CF_2OC_2F_4$	I 89 SmA -7 Cr	[3]

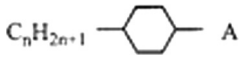
In the case of two-ring bicyclohexyl derivatives presented in Table 2, the terminal halogenation creates mainly the smectic phases. The presence of the ester or chlorine in the fluorinated end groups sometimes does not support the mesomorphic properties (compounds **2-4, 2-5,** and **2-7,** correspondingly). The introduction of the double carbon-carbon bonds in the terminal fluorinated groups usually stabilizes the mesophases (compounds **2-8, 2-11, 2-12, 2-23**). The perfluoropropenyl derivative **2-8** shows a slightly higher clearing temperature and a significantly lower melting point compared with those of the corresponding trifluoromethyl vinyl derivative **2-11**. The thermal data collated in Table 2 reveal that increasing the halogen content in the terminal groups enhances (compounds **2-8, 2-11; 2-13–2-15; 2-16–2-19**) and lowers (compounds **2-13–2-15, 2-16–2-19; 2-24–2-26**) the clearing points. The melting temperatures of these derivatives show a decrease (compounds **2-8, 2-11; 2-13–2-15; 2-16, 2-17, 2-19; 2-25, 2-26**) and a rise (compounds **2-15, 2-16, 2-17, 2-19; 2-14, 2-16, 2-17; 2-24, 2-26**), with increase of the halogen content. It is interesting that the methylenecyclohexyl derivatives do not exhibit any mesophases (compounds **2-20–2-22**).

For three-ring bicyclohexylphenyl derivatives (Table 3) increasing the fluorine content in the terminal perfluoroalkyl and perfluoroalkoxy groups mainly lowers (compounds **3-3–3-5; 3-6–3-8; 3-21, 3-22; 3-25, 3-27**) and enhances (compounds **3-9, 3-10**) the clearing temperatures. In some cases it leads to the disappearance of the mesophases (compounds **3-21, 3-25**). In the terminal groups containing the double carbon-carbon bonds, increasing the fluorine content enhances (compounds **3-12–3-14; 3-16, 3-17**) and lowers (compounds **3-12, 3-14; 3-30, 3-32**) the clearing points.

As it has been discovered earlier in [1], it is difficult to explain these and above discussed results in terms of the Maier – Saupe theory [39], 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 [40–42]) which in turns, according to Maier and Saupe [39], should enhance the stability of the mesophase. The melting temperatures of three-ring derivatives presented in Table 3 show a decrease (compounds **3-6–3-8; 3-12–3-14; 3-30, 3-32**) and increase (compounds **3-3–3-5; 3-16, 3-17; 3-21, 3-22; 3-25, 3-27**), with increase of fluorine content.

It is obvious from Table 3 that the introduction of the double bonds such as, carbon-carbon, keto, into the halogenated terminal groups usually enhances their thermal efficiency in comparison with corresponding parent and other groups (see for example, compounds **3-1, 3-20; 3-19, 3-28; 3-25, 3-26; 3-30, 3-31,** and reference

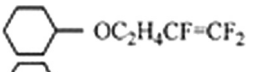
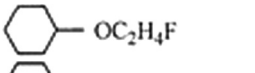
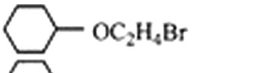
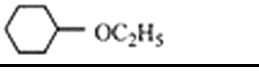
Table 2. Physico-chemical properties of liquid crystals:



No.	n	A	Phase transitions, °C	$\Delta\varepsilon^a$	Δn^a	η^b, mPas	Ref.
2-1	3	CF_3	Cr -5 SmB 69 I				[5]
			Cr l9 SmH? (8) SmB? 41 I	6.8[c]	0.059[c]		[6]
2-2	3	$OCOCF_3$	Cr 37.7 SmB 56.7 I	7.0	0.044	10.3	[7]
2-3	3	CH_2OCOCF_3	Sm 35.9 I				[7]
2-4	3	$C_2H_4OCOCF_3$	Cr 39.5 I	1.7	0.024	17.6	[7]
2-5	3	$OCOCHF_2$	Cr 68.9 I	6.3	0.037	15.6	[7]
2-6	3	$OCOC_2F_5$	Cr 25 Sm 43.2 I	9.0	0.030	13.6	[7]
2-7	3	$CF_2OCH_2CCl_3$	Cr 47 I	1.2[c]	0.049[c]		[8]
2-8	3	$CF{=}CFCF_3$	Cr 49.5 SmB 62.6 I	8.1	0.057		[9]
2-9	5	$CF_2OCH_2CF_3$	Cr 19 SmB 72 I	0.7[c]	0.050[c]	93[c,d]	[8]
2-10	3	$CH{=}C(CF_3)_2$	Cr 34 I	4.2	0.003		[10]
2-11	3	$CH{=}CHCF_3$	Cr 60 SmB 61 I	6.2[e]	0.051[e]		[6]
2-12	3	$CH{=}CHSF_5$	Cr 51 SmG? 65 I	10.5[c]	0.070[e]		[6]
2-13	3	C_3F_7	Cr 22 SmB 77 I	6.8[c]	0.062[c]		[11]
2-14	3	CF_2CHFCF_3	Cr 42 Sm (36) SmB 59 I	7.7[c]	0.059[c]		[11]
2-15	3	$CF_2CH_2CF_3$	Cr 76 I	6.6[c]	0.059[c]		[11]
2-16	3	$CF_2C_2H_5$	Cr 23 SmB 91.4 I				[12]
2-17	3	$CH_2CF_2CH_3$	Cr 23 SmB 91.4 I	8.3	0.111	13.0	[13]
2-18	3	$CHFCHFCH_3$	Cr 83 SmB 100 I	−2.9[f]			[14]
2-19	3	C_3H_7	Cr 65 SmB 83 I	−0.3[c]	0.043[c]		[11]
2-20	3	$=CF_2$	oil				[15]
2-21	3	$=CCl_2$	Cr 40 I				[15]
2-22	3	$=CHSF_5$	Cr 41 I	6.3[c]	0.063[c]		[6]

(*Continued*)

Table 2. Continued

No.	n	A	Phase transitions, °C	$\Delta\varepsilon^a$	Δn^a	η^b, mPas	Ref.
2-23	3		Cr 80 N (55) I				[16]
2-24	3		Cr 61 I				[16]
2-25	3		Cr 45 N (34) I				[16]
2-26	3		Cr 49 N 50 I				[17]

[a,b]Extrapolated from 15 wt% solution in liquid crystal material at 25°C and 20°C, respectively.
[c,f]Extrapolated from 10 wt% solution in ZLI-4792 and ZLI-2857 at 20°C, respectively.
[d]Rotational viscosity γ_1 [mPas].
[e]Extrapolated from 10 wt% solution in liquid crystal material at 20°C.

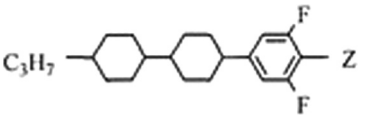
[43]). Sulphur-containing fluorinated groups usually show decreased values of clearing temperatures in comparison with those of the corresponding oxygen-containing fluorinated groups (compounds **3-3, 3-6; 3-23, 3-24, 3-29**). Similar trends have been found for other sulphur-containing groups [44]. The introduction of the oxygen atom into the halogenated groups usually enhances their thermal efficiency (compounds **3-3, 3-27; 3-4, 3-25**) which is supported by the findings for other oxygen-containing groups [45]. The additional alkoxy or alkyl groups, introduced between the terminal halogenated group and molecular core, can increase (compounds **3-1, 3-8; 3-2, 3-11; 3-6, 3-25, 3-31; 3-7, 3-27; 3-13, 3-17**) and lower (compounds **3-12, 3-16**) the clearing points.

Similar trends have been reported for other liquid crystals with the halogenated terminal groups [46–76] including axially fluoro substituted ones [77–89].

2.2. *Linking Substitution*

It is evident from Tables 4–6 that the introduction of the fluorinated linkages into the molecular structure of liquid crystals can enhance (compounds **4-1–4-5; 4-6, 4-9–4-11; 5-1, 5-8**) and lower (compounds **5-1–5-3, 5-12; 6-1–6-3; 6-8, 6-9, 6-11**) the clearing temperatures in comparison with those of the corresponding parent compounds and derivatives with the alkylene linkages. One can say that increasing the length of the polyfluorinated linking groups lowers the clearing points (compounds **4-2, 4-3; 4-13, 4-14**; see also similar results for the hydrocarbon derivatives **5-10** and **5-14**). Adding the methylene groups to difluoromethoxy one results in the disappearance of the mesophase, increasing and decreasing the clearing point for liquid crystals (LCs) having methylene-containing linkage and ethylene-containing one, respectively compared with that of the corresponding LCs with difluoromethoxy linkage (compounds **4-6, 4-7, 4-10; 5-8, 5-12; 6-2, 6-3**). These results are consistent with the low thermal efficiency of methylene linkage itself and can be explained in terms of its significant nonlinearity which is also responsible for low nematic thermostability of compound **4-8** with the CHFO linkage and non-mesomorphic behavior of compounds having the CF_2CF_2O linkage [114].

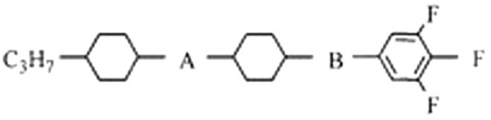
Table 3. Physico-chemical properties of liquid crystals:



No.	Z	Phase transitions, °C	$\Delta\varepsilon^a$	Δn^a	ν^a, min^2s^{-1}	Ref.
3-1	F	Cr 64.7 N 93.7 I	5.5[b]	0.078[b]	25.5[c,d]	[18]
		Cr 64.3 N 93.9 I	1.1.0[g]	0.079[g]		[19]
3-2	Cl	Cr 78 N 140 I	7.7	0.099	40.0	[20]
3-3	$OCHF_2$	Cr 62 N 128 I	8.8	0.082	29.0	[20]
3-4	OCF_3	Cr 63.8 N 99 I	15.0[g]			[9,21]
3-5	OCH_3	Cr 41 N 151.8 I		0.088		[22]
3-6	OCH_2CF_3	Cr 69 N 140 I		0.092		[22]
3-7	OCH_2CHF_2	Cr 72 N 152.9 I	7.8			[23]
3-8	OC_2H_4F	Cr 82 N 165.5 I	2.1			[22]
3-9	$OCH_2CF_2CHF_2$	Cr 70 N 127.2 I		0.087		[24]
3-10	$OCH_2C_2F_5$	Cr 66 SmA (48) N 130.5 I		0.082		[25]
3-11	OC_3H_6Cl	Cr 50 N 157.2 I	5.7			[22]
3-12	$CH{=}CF_2$	Cr 33 N 182.1 I				[26]
3-13	$CH{=}CH_2$	Cr 67 N 71 I				[27]
3-14	$CF{=}CF_2$	Cr 60 N 93 I		0.065		[28]
3-15	CF=CHCl	Cr 89 N 219.3 I				[28]
3-16	$OCH_2CH{=}CF_2$	Cr 72 N 172.3 I		0.090		[29]
3-17	$OCH_2CH{=}CH_2$	Cr 23.2 N 149.7 I				[25]
3-18	$CH_2CF{=}CH_2$	Cr 60 N 66 I				[30]
3-19	$OCF_2CF{=}CF_2$	Cr 41.2 N 166.6 I				[31]
3-20	COF	Cr 77 N 139 I	25.6[e]	0.106[f]	56[f]	[32]
3-21	CF_2CHF_2	Cr 82 I	10.9	0.074		[33]
3-22	$CHFCHF_2$	Cr 70 N 79.6 I	9.6	0.085		[33]
3-23	$SCHF_2$	Cr 70 N 84.4 I	9.8	0.086		[34]
3-24	SCH_2CF_3	Cr 91 N (65.1) I	3.9	0.085		[34]
3-25	CF_3	Cr 93 I	13.1			[35]
3-26	$COCF_3$	Cr 78 N 94.8 I	18.2	0.097		[36]
3-27	CHF_2	Cr 92 N 99.2 I	9.0			[37]
3-28	$CF{=}NCF_3$	Cr 89.3 N 119.1 I	24.3[g]			[9]
3-29	SO_2CF_3	Cr 146 I	25.8	0.100		[38]
3-30	$CH{=}CHCF_3$	Cr 106.9 N 170.6 I	19.4[g]	0.150[g]		[19]
3-31	$C_2H_4CF_3$	Cr_1 49.6 Cr_2 79.7 N 120.9 I	13.4[g]	0.090[g]		[19]
3-32	$CF{=}CFCF_3$	Cr 72.6 Sm 97.1 N 155.8 I	17.5[g]	0.110[g]		[19]

[a]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[b,c]Extrapolated from 20 wt% solution in liquid crystal material at 25°C and 20°C, respectively.
[d]Volume viscosity η [mPas].
[e,f]Extrapolated from the solution in liquid crystal material at 25°C and 20°C, respectively.
[g]Extrapolated from 15 wt% solution in liquid crystal material at 25°C.

Table 4. Physico-chemical properties of liquid corals:

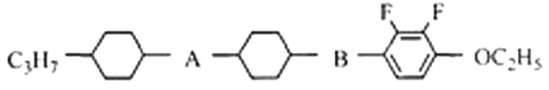


No.	A	B	Phase transitions, °C	$\Delta\varepsilon^a$	Δn^a	$\gamma_1{}^a$, mPas	Ref.
4-1	—	—	Cr 66 N 94.1 I	9.7	0.075	171	[90]
			Cr 64.7 N 93.7 I	5.5[b]	0.078[b]	25.5[c,d]	[18]
4-2	C_2F_4	—	Cr 70 SmG 95 SmB 102 N 168.6 I	9.0	0.060	269	[90]
4-3	C_4F_8	—	N 126 I[a]	8.7	0.064	370.0	[91]
4-4	CH=CH	—	Cr 51 N 101 I	11.4[e]	0.119[e]	51.8[d,f]	[92]
4-5	C_2H_4	—	Cr 45 N 81.71	9.4	0.076	212	[93,94]
			Cr 50.7 N 83.4 I	5.4[b]	0.077[b]	26.2[c,d]	[18]
4-6	—	CF_2O	Cr 42.9 N 105.5 I	9.8[g]	0.070[g]	184.8[g]	[95]
			Cr 44 N 105.3 I	10.5	0.067	145	[96]
4-7	—	CH_2CF_2O	Cr 58 I	3.1	0.046		[97]
4-8	—	CHFO	Cr 43 N 88 I	7.7	0.062	~300	[94,98]
4-9	—	C_2H_4	Cr 41.8 N 98.3 I	5.3[b]	0.078[b]	26.8[c,d]	[18]
4-10	—	$C_2H_4CF_2O$	Cr 68.6 N 113.1 I				[99]
4-11	—	C_2F_4	Cr 74 B 102 N 114.9 I	8.1		150	[94]
4-12	—	COO	Cr 56 114 N 117.2 I	11.1	0.067	175	[96]
4-13	C_4F_8	CF_2O	N 135 I[a]	9.1	0.076	340.0	[91]
4-14	C_2F_4	CF_2O	Cr 49 SmB 114 N 164.4 I	9.4	0.074	250.0	[90]

[a]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[b,c]Extrapolated from 20 wt% solution in liquid crystal material at 25°C and 20°C, respectively.
[d]Volume viscosity η [mPas].
[e,f]Extrapolated from 15 wt% solution in liquid crystal material at 25°C and 20°C, respectively.
[g]Extrapolated from 20 wt% solution in liquid crystal material at 20°C.

The fluorination of the ethylene and methoxy linkages results in increasing the melting and clearing points (compounds **4-9, 4-11; 5-8, 5-9**) and creation of the smectic B phase (compounds **4-9, 4-11**) while, the partial fluorination of the *trans*-stilbene group lowers the nematic thermostability and enhances the melting point (compounds **5-3, 5-4**). The effect of the distribution of the fluorine atoms in the linkage on the mesomorphic properties of LCs can be seen by comparing the data for compound **6-8** with the CH_2CF_2 linkage and compound **6-9** with the CHFCHF linkage, with the higher melting and clearing points and an appearance of the nematic phase observed for the latter. It has been demonstrated that an addition of the vinyl group to difluoromethoxy one enhances its thermal efficiency [106,115]. It can be seen from table 4 that moving the C_2F_4 linkage closer to the 3,4,5-trifluorophenyl fragment results in the disappearance of the smectic G phase and decreasing the nematic thermostability and range (compounds **4-2, 4-11**). While

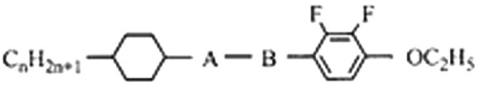
Table 5. Physico-chemical properties of liquid crystals:



No.	A	B	Phase transitions, °C	$\Delta\varepsilon^a$	Δn^b	$\gamma_1{}^b$, mPas	Ref.
5-1	—	—	Cr 79 SmB (78) N 184.5 I	−6.0	0.096	413.0	[100]
			Cr 76 SmB 79 N 186 I	−5.0[c]	0.074[c]	25.1[d,e]	[101]
5-2	CH_2CF_2	—	Cr l03 SmB (92) N 134.5 I	−6.6	0.100		[102]
5-3	CH=CF	—	Cr 98 SmB (45) N 181 I	−6.0			[102]
5-4	CH=CH	—	Cr 81 SmB (50) N 187.7 I	−5.9	0.105		[103]
5-5	CH=N	—	?	−6.5[c]	0.133[e]		[104]
5-6	$OCH_2CH=CH$	—	Cr 58.2 N 71.7 I	−4.1[c]	0.100[c]	62.9[d,e]	[105]
5-7	$CH=CHCH_2O$		Cr 79.3 N (68) I	−6.1[c]	0.107[c]	67.0[d,e]	[105]
5-8	—	CF_2O	Cr 70.3 N 191.7 I				[106]
5-9	—	CH_2O	Cr 62 N 154 I	−6.0[f]	0.120[f]	36.0[f,g]	[107]
5-10	—	C_2H_4	Cr 68 SmA 109 N 160 I	−3.7[f]	0.120[f]	34.0[f,g]	[107]
5-11	—	COO	Cr 87 SmB (8 l) SmA 98 N 222.1 I	−4.1[f]	0.110[f]	37.0[f,g]	[107]
5-12	—	$C_2H_4CF_2O$	Cr_1 47.4 Cr_2 51.9 SmA 99.5 N 164 I	−3.7[c]	0.100[c]	48.1[d,e]	[99]
5-13	—	CH_2S	Cr 74.1 SmB 85.6 N 89.4 I	−6.0[c]	0.114[c]		[108]
5-14	—	C_4H_8	Cr 44.4 SmA 107.2 N 129 I				[109]

[a]Extrapolated from 10 wt% solution in ZLI-2857 at 20°C.
[b]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[c,d]Extrapolated from 1.5 wt% solution in liquid crystal material at 25°C and 20°C, respectively.
[e]Volume viscosity η [mPas].
[f]Extrapolated from 10 wt% solution in ZLI-3086 at 20°C.
[g]Kinematic viscosity v [$min^2 s^{-1}$].

Table 6. Physico-chemical properties of liquid crystals:



No.	n	A	B	Phase transitions, °C	$\Delta\varepsilon^a$	Δn^a	η^b, mPas	Ref.
6-1	3		—	Cr 80 N 173.3 I	−5.9[c]	0.156[d]	233[d,c]	[100]
6-2	3		OCF_2	Cr 21.5 N 118 I	−5.6	0.134	46.3	[110]
6-3	3		$OCF_2C_2H_4$	Cr 51.2 N 98.1 I	−5.5	0.120	46.8	[110]
6-4	3		CF_2CH_2COO	?	−6.8	0.137		[111]
6-5	3		CH_2S	Cr 55.5 I	−4.6	0.140		[108]
6-6	3		C≡C	Cr 84 N 228.1 I	−5.2[c]	0.239[d]	263[d,e]	[112]
6-7	3		OC_3H_6	Cr 81.5 N 84.1 I	−4.1	0.120	69.0	[110]
6-8	5		CH_2CF_2	Cr 78 SmB 120.6 I				[102]
6-9	5		CHFCHF	Cr 80 SmB 145 N 164.5 I				[102]
6-10	5		SiH_2CH_2	Cr 46.8 SmA 111.2 I				[113]
6-11	5		—	Cr 66 SmB 125 N 184.8 I	−5.3[c]	0.091[d]	469[d,e]	[100]

[a,b]Extrapolated from 15 wt% solution in liquid crystal material at 25°C and 20°C, respectively.
[c]Extrapolated from 10 wt% solution in ZLI-2857 at 20°C.
[d]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[e]Rotational viscosity γ_1 [mPas].

similar move of the C_2H_4 linkage give the opposite results for the nematic phase (compounds **4-5, 4-9**).

It is evident from Table 4 that the introduction of two different fluorinated linkages into the molecular structure of liquid crystals significantly enhances the clearing temperatures compared with those of the parent compound (compounds **4-1, 4-13, 4-14**). The introduction of the second another fluorinated linkage into the molecular core of liquid crystals results in decreasing (compounds **4-2, 4-14**) and increasing (compounds **4-3, 4-13; 4-6, 4-13, 4-14**) the clearing temperatures. Tables 4–6 present also the liquid crystals with some well-known non-fluorinated linkages for comparison and better choosing the right components for the development of liquid crystal materials for display applications [116,117]. As in the case of terminally halogenated liquid crystals discussed above, it is difficult to explain some of presented results here in terms of Maier-Saupe theory [39].

Similar trends have been for other liquid crystals with halogenated linkages [73–76,95,101,118–149].

The presented results reveal that the terminal and linking halogenation of achiral liquid crystals may enhance and lower the thermal stability of the mesophases compared with that of corresponding hydrogenated and parent derivatives. The importance of the structure of liquid crystals, their substituents, and their halogen content and its distribution is also shown. It is believed that the electronic structure of halogenated groups [150–166] plays a very important role in the intra- and inter-molecular interactions [167–169] which affect the packing of the molecules, that predominantly influences mesophase stability [167–170]. Anisotropic dispersion interactions, and consequently the anisotropy of polarizability, depending on the electron density distribution in the groups under consideration, also influence the packing and hence the stability of the mesophases but play a secondary role compared to the steric factors [169]. Other molecular aspects such as the association [170] or dipole-dipole attraction in polar liquid crystalline derivatives, which can influence the packing of the molecules, also affect the stability of the mesophases [169]. Particularly, in perfluoroalkyl derivatives, the perfluoroalkyl group, which is more rigid and linear than the corresponding alkyl group [171–176] promotes microphase segregation [176–180] and strong electrostatic interactions, such as fluorophobic [171–174,176–184] and fluorophilic [183,185] interactions around the perfluoroalkyl groups, that can be responsible for the pronounced layer arrangements of molecules and phase formation [1].

3. Static Dielectric Properties

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$, where $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are, respectively, dielectric constants, that are parallel and perpendicular to the nematic director **n**; and molecular structure of liquid crystals is described by the theory of Maier and Meier [186]:

$$\Delta\varepsilon = \mathrm{NhF}/\varepsilon_{\mathrm{o}}[\Delta\alpha - \mathrm{F}\mu^2/\mathrm{kT}(1 - 3\cos^2\beta)]\mathrm{S}, \tag{1}$$

where $\mathrm{h} = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_{\|} + 2\varepsilon_{\perp})/3$; $\Delta\alpha = (\alpha_{\|} - \alpha_{\perp})$ 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 and N is the number of molecules per unit volume; S is the order parameter.

It is evident from Tables 2 and 3 that for the define molecular structure of liquid crystals, their dielectric anisotropy decreases approximately in the same sequence as the values of dipole moments for the terminal groups diminish [1]. While, the total dipole moment and consequently, the dielectric anisotropy of compounds presented in Tables 4–6 are strongly affected by values and directions of the dipole moments of the fluorinated linkages (see Eq. 1).

4. Optical Properties

The phenomenological relation between the refractive index and the electric polarization is defined as [187,188]:

$$(\mathrm{n}^{*2} - 1)/(\mathrm{n}^{*2} + 2) = \mathrm{N}\alpha^*/3\varepsilon_{\mathrm{o}}, \tag{2}$$

where the mean polarizability $\alpha^* = (\alpha_{\|} + 2\alpha_{\perp})/3$; the mean refractive index $\mathrm{n}^{*2} = (\mathrm{n}_{\mathrm{e}}^2 + 2\mathrm{n}_{\mathrm{o}}^2)/3$; n_{o} is the ordinary and n_{e} is the extraordinary refractive indices.

Tables 2 and 3 show that the halogenated compounds exhibit similar values of optical anisotropy ($\Delta n = n_e - n_o$) to those of other halogenated LCs presented in [1]. While, a decrease in optical anisotropy for compounds with the fluorinated linkages (compounds **4-1, 4-2, 4-3, 4-6–4-8,** Tables 4–6) 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 linking halogen(s) substituted liquid crystals than for the corresponding parent compounds or having hydrogenated linkages [1,189–192].

5. Viscosity

It has been demonstrated that the nematic liquid crystalline materials for display applications should have a low viscosity for giving the acceptable response times to liquid crystal displays [193,194]. The rotational viscosity γ_1 of a nematic liquid crystal (NLC) is a dissipative coefficient describing the rate of reorientation of the NLC director [195]. The magnitude of the rotational and flow viscosities depend on molecular structure, inter-molecular association, and temperature [196,197]: as temperature increases, viscosity decreases [196–199]. It can be seen from Table 4 that the introduction of the fluorinated linkages into the molecular core of liquid crystals can enhance (compounds **4-1, 4-2, 4-3; 4-8, 4-13, 4-14**) and lower (compounds **4-1, 4-6, 4-11**) their viscosity. Increasing the fluorine content in the linkages enhances (compounds **4-2, 4-5**) and lowers (compounds **4-6, 4-8**) the viscosity. Increasing the length of the fluorinated linkages introduced into the molecular core of liquid crystals enhances their viscosity (compounds **4-2, 4-3; 4-13, 4-14; 6-2, 6-3,** Tables 4 and 6). It is evident from Table 5 that an addition of the CF_2O group to the C_2H_4 linkage increases the viscosity of liquid crystals (compounds **5-10, 5-12**). Moving the C_2F_4 linkage closer to the 3,4,5-trifluorophenyl fragment lowers the rotational viscosity of liquid crystals (compounds **4-2, 4-11,** Table 4). While, the introduction of the second fluorinated linkage into the molecular core of liquid crystals significantly increases their rotational viscosity (compounds **4-6, 4-13, 4-14,** Table 4).

6. 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 the observed properties. The information here presented may lead to a better understanding of the nature of liquid crystals.

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