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Vladimir F. Petrov [a b] & Yo Shimizu [a]

[a] Department of Organic Materials, Osaka National Research Institute, 1-8-31 Midorigaoka, Ikeda, Osaka, 563-8577, Japan

[b] LC Works, 6/68 Brinsley Road, Camberwell, VIC. 3124, Australia

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Perfluoro(Alkoxy)Alkylation in Achiral Liquid Crystalline Ester Derivatives

VLADIMIR F. PETROV* and YO SHIMIZU

Department of Organic Materials, Osaka National Research Institute, 1–8–31 Midorigaoka, Ikeda, Osaka 563–8577, Japan

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The effect of perfluoro(alkoxy)alkyl groups on the appearance of the mesophases and their physico – chemical properties in achiral liquid crystalline ester derivatives is discussed and compared with that of the corresponding (alkoxy)alkyl groups.

Keywords: perfluoro(alkoxy)alkyl groups; physico-chemical properties; liquid crystals

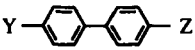
1. INTRODUCTION

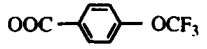
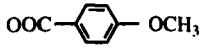
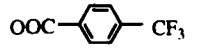
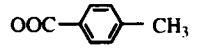
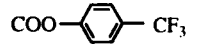
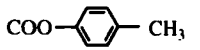
Over the past two decades there has been shown much interest in the design and synthesis of liquid crystalline ester derivatives,[1–15] particularly perfluoro(alkoxy)alkyl substituted ones owing to their remarkable physico-chemical and electro-optical properties.[16–24] As a part of our systematic studis of the structure-property relations in liquid crystals {see, for example our previous publications which discuss the effects of perfluoroalkylation in one-ring ester derivatives[19–23]}, we present here our results of the study on the effect perfluoro(alkoxy)alkyl groups in two- and three-ring ester derivatives on their mesomorphism and the physico – chemical properties. The results of this study will be compared with those of the corresponding derivatives having (alkoxy)alkyl groups.

* Author for correspondence. Present address: LC Works, 6/68 Brinsley Road, Camberwell, VIC. 3124, Australia.

2. PHYSICO – CHEMICAL PROPERTIES

The phase transition temperatures of some perfluoro(alkoxy)alkyl substituted ester derivatives and the corresponding (alkoxy)alkyl substituted reference compounds are summarized in tables I–VII, where Cr, SmA, SmB, SmC, N and I are the crystalline, smectic A, smectic B, smectic C, nematic and isotropic phase, respectively.

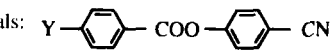
TABLE I Mesomorphic properties of liquid crystals: 

No.	*Y*	*Z*	*Phase transitions, °C*	*Ref.*
1–1	C_6F_{13}	H	Cr 69 I	(25)
1–2	$C_6F_{13}C_2H_4COO$	H	Cr 80.5 SmA 113.2 I	(26)
1–3	$C_6F_{13}C_2H_4OOC$	H	Cr 70.5 SmA 72 I	(27)
1–4	C_6F_{13}	CN	Cr 101 I	(25)
1–5	$C_6F_{13}C_2H_4COO$	CN	Cr 92 SmA 161 I	(26)
1–6	$C_6F_{13}C_2H_4OOC$	OC_8H_{17}	Cr 114 SmC 125 SmA 127 I	(30)
1–7	$C_6F_{13}CH_2OOC$	OC_8H_{17}	Cr 85 SmC 109 SmA 116 I	(30)
1–8	$HC_6F_{12}CH_2OOC$	OC_8H_{17}	Cr 74.3 SmA 81.2 I	(31)
1–9	$C_8H_{17}OOC$	OC_8H_{17}	Cr 80 SmA 80 I	(32)
1–10	$C_7H_{15}OOC$	OC_8H_{17}	Cr 87 SmC (46) SmA (83) I	(32)
1–11	$C_8H_{17}O$		Cr 114 SmB 140 SmA 217 I	(8)
1–12	$C_8H_{17}O$		Cr 123 N 218 I	(8)
1–13	$C_8H_{17}O$		Cr 134 SmB 152 SmA 217 I	(8)
1–14	$C_8H_{17}O$		Cr 131 N 195 I	(8)
1–15	$C_8H_{17}O$		Cr 132 SmB 142 SmA 217 I	(8)
1–16	$C_8H_{17}O$		Cr 115 SmB (110) SmA 184 N 199 I	(8)

It is evident from table I that the perfluoroalkylation of the biphenyl fragment does not creates the mesophases {compound **1–1** and the reference[25]}. The

smectic phases can be formed in these derivatives by attaching the perfluoroalkyl group to the biphenyl core through the ester connector (compounds **1–2**, **1–3**) and other connectors.[28,29] The importance of the orientation of ester groups, which form the connectors, is illustrated by comparing the phase transition temperatures of compounds **1–2** and **1–3**, with a higher efficiency observed for the former compound containing C_2H_4COO connector. Similar results have been found for 4, 4′-disubstituted biphenyl derivatives presented in table I (compounds **1–4** and **1–5**; **1–6** and **1–9**; **1–7**, **1–8** and **1–10**). Perfluorohexyl substituted derivatives **1–6** and **1–7** exhibit higher smectic A thermostabilities and higher (compound **1–6**) and lower (compound **1–7**) melting temperatures in comparison with those of the corresponding alkyl substituted derivatives **1–9** and **1–10**, respectively. While decreasing the fluorination content of compound **1–7** lowers the melting and clearing points (compound **1–8**). Interestingly, comparing the phase transition temperatures of compounds **1–8** and **1–10** in terms of fluorination content of their terminal substituents, we can point out that increasing the fluorination content leads to decreasing the melting and clearing temperatures.

As can be seen from table I, increasing the length of the connectors results in increasing the crystal – smectic C, smectic C – smectic A, smectic A – isotropic phase transition temperatures (compounds **1–6** and **1–7**).

TABLE II Mesomorphic properties of liquid crystals: 

No.	*Y*	*Phase transitions, °C*	*Reference*
2–1	C_3F_7	Cr 93 I	(33)
2–2	C_4F_9	Cr 82.5 Sm (80) I	(33)
2–3	C_5F_{11}	Cr 100 Sm 123 I	(33)
2–4	C_6F_{13}	Cr 100 Sm 124 I	(34)
2–5	C_7F_{15}	Cr 104 Sm 136 I	(33)
2–6	$CF_3C_2H_4$	Cr 99 Sm (57) I	(35)
2–7	$CF_3C_3H_6$	Cr 74 I	(35)
2–8	C_3H_7	Cr 103.5 N (51.4) I	(1)
2–9	C_4H_9	Cr 66.1 N (41.4) I	(1)
2–10	C_5H_{11}	Cr 64.4 N (55.4) I	(1)
2–11	C_6H_{13}	Cr 44.4 N 48.6 I	(1)
2–12	C_7H_{15}	Cr 44 N 56.5 I	(1)
2–13	C_4F_9O	Cr 80 Sm 128 I	(34)
2–14	C_4F_8HO	Cr 74 Sm 94 I	(34)
2–15	$C_3F_7CH_2O$	I 58 SmA 43 Cr	(36)
2–16	C_4H_9O	Cr 92 N 104 I	(1)

TABLE III Mesomorphic properties of liquid crystals: Y—⬡—A—COO—⬡—Z

No.	*Y*	*A*	*Z*	*Phase transitions, °C*	*Ref.*
3–1	C_4F_9	-	CN	Cr 84 Sm 99 I	(33)
3–2	C_5F_{11}	-	CN	Cr 92 Sm 118 I	(33)
3–3	C_6F_{13}	-	CN	Cr 101 Sm 151 I	(33)
3–4	C_7F_{15}	-	CN	Cr 101 Sm 153 I	(33)
3–5	$CF_3C_3H_6$	-	CN	Cr 62 I	(35)
3–6	C_4H_9	-	CN	Cr 54.7 N 69.9 I	(37)
3–7	C_5H_{11}	-	CN	Cr 47.4 N 79.5 I	(37)
3–8	C_6H_{13}	-	CN	Cr 49.5 N 77 I	(38)
3–9	C_7H_{15}	-	CN	Cr 54 N 82.5 I	(38)
3–10	C_7F_{15}	-	OC_8H_{17}	Cr 104 Sm 120.3 SmA 145.6 I	(39)
3–11	C_7H_{15}	-	OC_8H_{17}	Cr 44 SmG (15) SmB 65.5 SmA 77 N 80.5 I	(40)
3–12	$C_4F_9C_2H_4OOC$	-	C_8H_{17}	Cr 55 SmA (53) I	(18)
3–13	$C_6H_{13}OOC$	-	C_8H_{17}	Cr 39 SmA (37) I	(18)
3–14	C_5H_{11}	⬡	OCF_3	Cr 106 SmB (84) SmA 131 N 167.9 I	(46)
3–15	C_5H_{11}	⬡	OCF_2H	Cr 87 SmB (69) SmA 96 N 177.9 I	(46)
3–16	C_5H_{11}	⬡	OCH_3	Cr 122.5 N 212 I	(47)

Tables II–IV present the phase transition temperatures of two-ring derivatives with ester linking groups. It is evident from tables II, III and the reference[34] that the perfluoro(alkoxy)alkylation of the 4-cyanophenyl derivatives increases (compounds **2–2** and **2–9, 2–3** and **2–10, 2–4** and **2–11, 2–5** and **2–12, 3–1** and **3–6, 3–2** and **3–7, 3–3** and **3–8, 3–4** and **3–9**) the clearing and melting points, decreases (compounds **2–1** and **2–8**) the clearing and melting temperatures and increases the clearing points and lowers the melting temperatures (compounds **2–13** and **2–16**). It is important to note that the perfluoro(alkoxy)alkylation of the cyano derivatives, showed in tables II, III and the reference,[34] leads to the disappearance of the nematic phases and creation of only smectic phases. Particularly, the perfluoroalkylation results in the disappearance of odd-even effect in the clearing points (compounds **2–2 – 2–5** and **2–9 – 2–12, 3–1 – 3–4** and **3–6 – 3–9**), and enhances the smectic thermostability with increasing the length of per-

fluoroalkyl groups. Decreasing the fluorination content of perfluoro(alkoxy)alkyl groups increases (compounds **2–1** and **2–6**) and lowers (compounds **2–13** and **2–14**, **2–15**) the clearing points, and leads to the disappearance of the mesophases (compounds **2–2** and **2–7**, **3–1** and **3–5**, compare with the corresponding nematic derivatives **2–9**, **3–6**). As it has been shown for alkoxy and alkyl substituted 4-cyanophenyl benzoates,[1,2] perfluoroalkoxy substituted cyano derivatives exhibit higher clearing temperatures in comparison with those of the corresponding perfluoroalkyl substituted cyano derivatives {compounds **2–2** and **2–13**, the references [33,34]}.

TABLE IV Mesomorphic properties of liquid crystals: 

No.	*Y*	*Z*	*Phase transitions, °C*	*Reference*
4–1	$C_8F_{17}C_2H_4O$	OC_6H_{13}	Cr 106 SmC 131 SmA 169 I	(41)
4–2	$C_{10}H_{21}O$	$OC_2H_4C_4F_9$	I 114 SmA 79 SmC 56 Cr	(36)
4–3	$C_{10}H_{21}O$	$OCH_2C_5F_{11}$	I 93 SmA 78 SmC 53 Cr	(36)
4–4	$C_{10}H_{21}O$	OC_6H_{13}	Cr 62.5 SmE (38) SmB (44.5) SmC 77.5 SmA 83.3 N 88.9 I	(40)
4–5	$C_{10}F_{21}$	OC_6H_{13}	Cr 134 SmA 143 I	(42)
4–6	$C_{10}H_{21}$	$OCH_2C_5F_{11}$	I 82 SmA 59 SmC 47 Cr	(36)
4–7	$C_{10}H_{21}$	OC_6H_{13}	Cr 44.1 SmB (33.6) SmA 47.7 N 59 I	(43)
4–8	CF_3	OC_6H_{13}	Cr 84 I	(16)
4–9	CH_3	OC_6H_{13}	Cr 81 I	(16)
4–10	CF_3O	OC_6H_{13}	Cr 43 Sm 110 N 138 I	(16)
4–11	HCF_2O	OC_6H_{13}	Cr 56 N 58 I	(16)
4–12	CH_3O	OC_6H_{13}	Cr 55 N 79 I	(16)
4–13	C_2F_5O	OC_6H_{13}	Cr 61 Sm 94 N 102 I	(16)
4–14	CF_3CH_2O	OC_6H_{13}	I 88 SmA 82 Cr	(36)
4–15	C_2H_5O	OC_6H_{13}	Cr 83 N 98 I	(16)

Similar results have been found for weakly polar derivatives which show the enhanced clearing and melting points and reduced number of the mesophases for perfluoroalkyl substituted derivatives **3–10**, **4–5** in comparison with those of the corresponding alkyl substituted compounds **3–11**, **4–7**. While increasing the fluorination content of the terminal groups increases (compounds **4–1** – **4–3** and **4–4**, **4–6** and **4–7**, table IV) and lowers (compounds **4–2** and **4–3**) the clearing temperatures. The melting temperatures show similar increasing (compounds **4–1** and **4–4**, **4–6** and **4–7**) and decreasing behavior (compounds **4–2**, **4–3** and **4–**

4). Interestingly, the partial fluorination of one of two terminal substituents of compound **4–4** lowers the number of the mesophases (compounds **4–1** – **4–3**). The thermal data collated in table IV reveals that the replacement of hydrogen atoms by fluorine atoms in the terminal methyl group of compound **4–9** to give trifluoromethyl substituted derivative **4–8** does not change its non-mesomorphic behavior, leading to an increase of the melting point.

TABLE V Mesomorphic properties of liquid crystals: Y–⟨⟩–COO–⟨⟩–Z

No.	*Y*	*Z*	*Phase transitions, °C*	*Ref.*
5–1	$C_8H_{17}O$	$COOCH_2C_2F_5$	Cr 48 SmC 68 SmA 84 I	(18)
5–2	$C_8H_{17}O$	$COOCH_2C_2F_4H$	Cr 76 SmC (37) SmA (58) I	(18)
5–3	$C_8H_{17}O$	$COOC_3H_7$	Cr 52.2 SmA 79.8 I	(40)
5–4	$C_8H_{17}O$	$COOC_2H_4C_4F_9$	Cr 71 SmC 109 SmA 111 I	(18)
5–5	$C_8H_{17}O$	$COOC_6H_{13}$	Cr 51 SmA 69 I	(18)
5–6	$C_8H_{17}O$	$COOCH_2C_6F_{13}$	Cr 71 SmC 107 SmA 120 I	(18)
5–7	$C_8H_{17}O$	$COOC_2H_4C_6F_{13}$	Cr 88 SmC 122 SmA 129 I	(18)
5–8	$C_4F_9C_4H_8O$	$COOC_2H_4C_6F_{13}$	Cr 126.3 SmC (114.7) SmA (118.5) I	(44)
5–9	$C_8H_{17}O$	$COOCH_2C_4F_8H$	Cr 61 SmC (59) SmA 68 I	(18)
5–10	$C_4F_9C_4H_8O$	$COOCH_2C_4F_8H$	Cr 90.1 SmC (65) SmA (76.2) I	(44)
5–11	$C_8H_{17}O$	$COOC_5H_{11}$	Cr 52 SmA 69 I	(40)
5–12	$C_4F_9C_2H_4OOC$	OC_8H_{17}	Cr 87 SmA 96 I	(19)
5–13	$C_6H_{13}OOC$	OC_8H_{17}	Cr 57 I	(19)
5–14	$C_8F_{17}C_2H_4OOC$	OC_8H_{17}	Cr 116 SmA 136 I	(18)
5–15	$C_8F_{17}C_2H_4O$	OC_8H_{17}	Cr 104 SmC 138 SmA 162 I	(41)

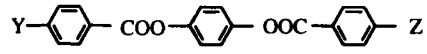
It should be mentioned that the partial fluorination of the terminal methoxy group sufficiently lowers the nematic thermostability and slightly increases the melting temperature (compounds **4–11** and **4–12**). While its full fluorination significantly decreases the melting point, increases the clearing temperature, and creates an additional smectic phase (compounds **4–10** and **4–12**). Similar results have been observed for compounds **4–13** – **4–15**, the only difference is only smectic phase showed by the partially fluorinated derivative **4–14**.

It is evident from tables III, V that the partial fluorination of one of the terminal substituents of two-ring derivatives, which have the ester groups in the terminal and linking positions, results in increasing (compounds **3–12** and **3–13, 5–1** and **5–2, 5–4** and **5–5, 5–12** and **5–13**) and decreasing (compounds **5–2** and **5–3, 5–9** and **5–11**) the clearing temperatures. The melting temperatures show similar

increasing (compounds **3–12** and **3–13, 5–2** and **5–3, 5–4** and **5–5, 5–9** and **5–11, 5–12** and **5–13**) and decreasing (compounds **5–1** and **5–3**) behavior. Increasing the fluorination content of the second terminal substituent of perfluoroalkyl substituted phenyl benzoates lowers (compounds **5–7** and **5–8**) and enhances (compounds **5–10** and **5–11**) the smectic thermostabilities and leads to increasing the melting temperatures. These corresponds to a decrease of the ratio d / L, where d is the layer spacing defined from X-ray diffraction experiments and L is the molecular length.[44,45]

As in the case of the biphenyl derivatives discussed above, increasing the length of the connector increases the phase transition temperatures (compounds **5–6** and **5–7**). The importance of its structure is revealed by consideration of the phase transition temperatures of compounds **5–14** and **5–15**, with lower smectic A thermostability, higher melting point and reduced number of the mesophases recorded for the former derivative having ester connector {see also the reference[27]}.

TABLE VI Mesomorphic properties of liquid crystals:



No.	*Y*	*Z*	*Phase transitions, °C*	*Ref.*
6–1	$C_8H_{17}O$	CF_3	Cr 190 SmA 212 I	(48)
6–2	$C_8H_{17}O$	CH_3	Cr 102 N 199 I	(9)
6–3	$C_8H_{17}O$	OCF_3	Cr 149 SmA 203 N 209 I	(9, 48)
6–4	$C_8H_{17}O$	OCF_2H	Cr 142 SmC 163 SmA 210 I	(49)
6–5	$C_8H_{17}O$	OCH_3	Cr 124 N 224 I	(9)
6–6	$C_8H_{17}O$	$OCH_2C_3F_7$	I 200 N 187 SmC 110 Cr	(36)
6–7	$C_7F_{15}CH_2O$	$OCH_2C_3F_7$	I 254 N 205 SmC 88 Cr	(36)
6–8	$C_8H_{17}O$	OC_4H_9	Cr 121 N 214 I	(50)
6–9	CF_3	CF_3	Cr 174 Sm 221 I	(16)
6–10	CH_3	CH_3	Cr 220 N 228 I	(16)
6–11	CF_3O	OCF_3	Cr 135 Sm 162 N 193 I	(16)
6–12	HCF_2O	OCF_2H	Cr 175 N 200 I	(16)
6–13	CH_3O	OCH_3	Cr 222 N 300 I	(16)
6–14	C_2F_5O	OC_2F_5	Cr 199 Sm 257 N 263 I	(16)
6–15	C_2H_5O	OC_2H_5	Cr 226 N 287 I	(16)

It has been reported that the change of the orientation of ester linking group of compound **5–14** results in increasing the clearing temperatures.[19] It corre-

sponds to lowering the ratio d / L (from 1.10 to 1.00 at $T_{meas} = T_{cl} - 25$ °C, where T_{cl} is the smectic-isotropic phase transition temperature).[19] These results reveal the change from partially bilayer to monolayer structure of the smectic A phase of these compounds.

The phase transition temperatures of three-ring ester derivatives presented in tables I, III, VI, VII show that the terminal OCF_3 substitution is less thermally effective and is more pronounced in the formation of smectic phases than the corresponding OCH_3 substitution (compounds **1–11** and **1–12, 3–14** and **3–16, 6–3** and **6–5, 7–3** and **7–4, 7–7** and **7–8**). However, the change of the orientation of ester linkages results in the opposite situation in the clearing temperatures (compounds **7–9** and **7–10**). The melting temperatures also show the increased (compound **6–3** and **6–5, 7–3** and **7–4, 7–7** and **7–8, 7–9** and **7–10**) and decreased (compounds **1–11** and **1–12, 3–14** and **3–16**) values for the OCF_3 derivatives in comparison with those of the corresponding OCH_3 derivatives. The results which are found for the OCF_3 substituted derivative **7–3** and the corresponding OCH_3 substituted derivative **7–4** correspond to an increase of the ratio d / L observed for the former compound in comparison with that of the latter compound. The replacement of one fluorine atom in the terminal OCF_3 group to obtain OCF_2H group increases the clearing temperatures and lowers the melting points (compounds **3–14** and **3–15, 6–3** and **6–4**). The terminal trifluoromethyl substitution is more efficient and gives higher melting temperatures and more pronounced character of the smectic phases than the corresponding methyl substitution (compounds **1–13** and **1–14, 1–15** and **1–16, 6–1** and **6–2, 7–1** and **7–2, 7–5** and **7–6**). The terminal OCF_3 group is more efficient than the CF_3 group (compounds **7–1** and **7–3**), while changing the orientation of ester linkages leads to the opposite behavior (compounds **6–1** and **6–3, 7–5** and **7–7**). The CF_3 and OCF_3 terminal groups can show the same thermal efficiency for three-ring compounds which have the single carbon-carbon bond as a linking group A and OOC ester linkage as a linking group B (compounds **1–11** and **1–13**). The melting temperatures show higher values for CF_3 substituted derivatives than for the corresponding OCF_3 substituted compounds (compounds **1–11** and **1–13, 6–1** and **6–3, 7–1** and **7–3, 7–5** and **7–7**). These results correspond to the increased values of the ratio d / L for the former derivatives {compounds **6–1** and **6–3, 7–1** and **7–3, 7–5** and **7–7** and the reference[53]}.

The influence of the terminal CF_3 and OCF_3 groups attached to the core of three-ring ester derivatives on the efficiency of their ester linking groups (A-B) (compounds **1–11, 1–12, 1–15, 6–1, 6–3, 7–1, 7–3, 7–5, 7–7, 7–9**, tables I, VI, VII) can be expressed by the following orders of increasing the clearing tempera-

tures T_{cl} (nematic-isotropic or smectic-isotropic phase transition temperatures) and melting temperatures T_m (crystal-smectic phase transition temperatures):
For the CF_3 derivatives

$T_{cl} \rightarrow$ A-B: OOC-OOC < COO-OOC < COO-COO < SB-OOC = SB-COO
$T_m \rightarrow$ A-B: COO-COO < OOC-OOC < SB-COO < SB-OOC < COO-OOC

For the OCF_3 derivatives

$T_{cl} \rightarrow$ A-B: OOC-OOC < COO-OOC < COO-COO < SB-OOC < OOC-COO
$T_m \rightarrow$ A-B: OOC-OOC < SB-OOC < COO-COO < COO-OOC < OOC-COO,

where SB is the single carbon-carbon bond. These results reveal the different influence of the terminal CF_3 and OCF_3 groups on the efficiency of ester linkages, while the OOC-OOC combination of ester groups shows the lowest thermal efficiency for both terminal substituents.

Interestingly, the ratio d / L depends on the structure of two ester linking groups (A-B), which can be expressed as follows (table VII):

For the CF_3 derivatives d / L $\rightarrow$ A-B: COO-COO < COO-OOC < OOC-OOC

For the OCF_3 derivatives d / L $\rightarrow$ A-B: OOC-COO < COO-COO < COO-OOC

Again, we see the different influence of the terminal CF_3 and OCF_3 substituents on the efficiency of ester linkages in the formation of smectic A phase.

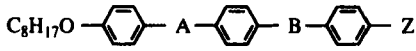
As it was observed above for two-ring derivatives, increasing the fluorination content of the terminal substituents of three-ring ester derivatives lowers the nematic thermostability and the melting point (compounds **6–6** and **6–8**, table VI) and gives rise to the melting and clearing temperatures (compounds **7–11** and **7–12**, table VII). Non-symmetrical partial fluorination of both terminal groups lowers the melting temperature and enhances the nematic thermostability (compounds **6–7** and **6–8, 6–6** and **6–7**). As can be seen from table VI, the symmetrical di-perfluoro(alkoxy)alkylation of both terminal substituents attached to the molecular core of three-ring ester derivatives leads to decreasing the melting and clearing temperatures and forms the smectic phases (in some cases) in comparison with those of the corresponding di-(alkoxy)alkyl derivatives (compounds **6–9** and **6–10, 6–11** and **6–13, 6–14** and **6–15**). While decreasing the fluorination content of these groups enhances the liquid crystal properties (compounds **6–11** and **6–12**).

The results of this study reveal the importance the structure of the perfluoro(alkoxy) alkyl groups and ester derivatives in the formation of the mesophases and their thermal properties.

Similar results have been reported for other liquid crystalline ester derivatives.[54–65] It has been shown that the perfluoroalkyl group, which is more rigid and linear than the corresponding alkyl one,[18–20, 30, 42] promotes the micro-

phase segregation,[29, 42, 59, 66, 67] and the strong electrostatic interactions, such as fluorophobic[18–23, 29, 42, 59, 66, 67] and fluorophilic[23, 51] interactions around the perfluoro(alkoxy)alkyl groups, can be responsible for the pronounced layer arrangements of molecules and phase formation of achiral perfluoro(alkoxy)alkyl substituted ester derivatives.

TABLE VII Physico-chemical properties of liquid crystals:



No.	*Z*	*A*	*B*	*Phase transitions, °C*	d^a, Å	d^a / L	*Ref.*
6–1	CF_3	COO	OOC	Cr 190 SmA 212 I	31.6	1.068	(48)
6–3	OCF_3	COO	OOC	Cr 149 SmA 203 N 209 I	32.2	1.042	(9, 48)
7–1	CF_3	COO	COO	Cr 126 SmA 213 I	30.8	1.041	(48)
7–2	CH_3	COO	COO	Cr 109 SmA 134 N 195 I			(9)
7–3	OCF_3	COO	COO	Cr 122 SmA 216 I	32.1	1.039	(48)
7–4	OCH_3	COO	COO	Cr 107 SmA 122 N 226 I	30.7	1.003	(9, 48)
7–5	CF_3	OOC	OOC	Cr 128 Sm (118) SmA 210 I	31.5	1.079	(51)
7–6	CH_3	OOC	OOC	Cr 112 N 189 I			(9)
7–7	OCF_3	OOC	OOC	Cr 108 SmA 208 I	31.8	1.053	(48)
7–8	OCH_3	OOC	OOC	Cr 101 N 214 I			(9)
7–9	OCF_3	OOC	COO	Cr 193 SmA 225 I	31.5	1.026	(48)
7–10	OCH_3	OOC	COO	Cr 167 N 218 I			(9)
7–11	Z_1	–	COO	Cr 106.4 SmC 179.4 SmA 197.9 I			(31)
7–12	Z_2	–	COO	Cr 66 SmC 138 SmA 192 I			(52)

a. $T_{meas} = T_{SmA\text{-}N}$ or $T_{SmA\text{-}I} - 10$ °C $Z_1 = COOCH_2C_4F_8H$ $Z_2 = COOC_5H_{11}$.

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:[68]

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

where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_| + 2\varepsilon_\perp)/3$; $\Delta\alpha = (\alpha_| - \alpha_\perp)$ 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 has been shown that the replacement of two hydrogen atoms by two fluorine atoms in the terminal OCH_3 group to give $OCHF_2$ group results in increasing the dielectric anisotropy of liquid crystals due to the dipole moment being increased from 1.25 to 2.46 D[17,69] {see equation 1}.

Compound **3–15**: $\varepsilon_\perp = 4.8$, $\Delta\varepsilon = 7.3$, $\tau = 0.98 = T_{meas} / T_{cl}$, K Reference[17]

Compound **3–16**: $\varepsilon_\perp = 3.4$, $\Delta\varepsilon = 0.3$, $\tau = 0.94$ Reference[47]

Similar results have been found for other liquid crystalline ester derivatives.[17, 46, 58]

4. CONCLUSION

Systematic studies of the effect of perfluoro(alkoxy)alkyl groups on the creation of the mesophases and their physico-chemical properties in achiral ester derivatives 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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