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Liquid Crystals

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Liquid crystalline 1,4-disubstituted cyclohexenylene derivatives

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The influence of the positions of the 1,4-cyclohexenylene fragment and its carbon-carbon double bond in the molecular core, on the mesomorphic behaviour and physical properties of 1,4-disubstituted cyclohexenylene derivatives is discussed and rationalized in terms of existing theories.

1. Introduction

Liquid crystalline 1,4-disubstituted cyclohexenylene derivatives have aroused considerable interest in recent years owing to their remarkable mesomorphic and physical properties [1–18]. Clearly, there is a close relationship between the molecular structure of these compounds and their properties. On the other hand, a clear description of the driving force of these phenomena is still lacking, and for this purpose, we would like to report an investigation of the structure–property relationships involved in 1,4-disubstituted cyclohexenylene derivatives in relation to nematic display applications. It is believed that only this approach can lead to a rational design of liquid crystals with optimized features. It would be interesting not only to estimate the effect of the positions of the 1,4-cyclohexenylene fragment and its double bond, but also to estimate the effect on mesomorphic and physical properties of replacing this fragment, having a double bond with a highly polarizable π-electron system, by the saturated *trans*-1,4-cyclohexane molecular fragment.

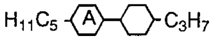
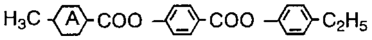
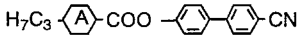
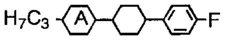
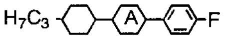
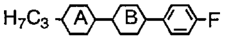
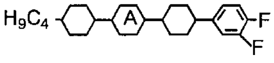
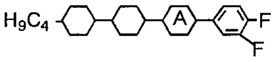
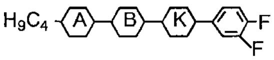
The range of compounds studied is indicated in table 1, where different molecular core structures are identified by a 'system' number.

2. Mesomorphic properties

The effect on mesomorphic properties of the presence and position of the 1,4-cyclohexylene fragment and its carbon-carbon double bond in the molecular core of various liquid crystals is shown in tables 2–5.

Weakly polar compounds such as 4-*n*-pentyl-1-cyclohexene-1-carboxylic acid and *trans*-4-*n*-pentyl-2-cyclohexene-1-carboxylic acid exhibit very interesting mesomorphic behaviour (compounds **1-1**, **1-2**, table 2). One can expect that the replacement of the *trans*-1,4-cyclohexylene fragment in compound **1-3** by the 1,4-cyclohex-1-enylene or *trans*-1,4-cyclohex-2-enylene fragments having a double bond with a highly polarizable π-system, to produce compounds **1-1** and **1-2** with an increase in

Table 1. Liquid crystal compound systems.

Structure	System number	Reference
	(1)	[1, 2, 19]
	(2)	[6, 20]
	(3)	[1, 9]
	(4)	[1, 21]
	(5)	[14, 22]
	(6)	[14, 15, 22]
	(7)	[14, 15, 22]
	(8)	[13, 16]
	(9)	[13, 16]
	(10)	[13, 16]

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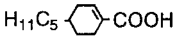
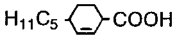
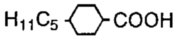
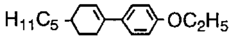
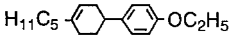
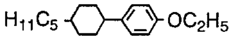
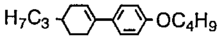
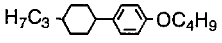
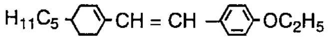
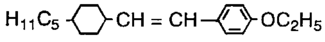
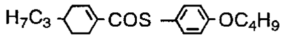
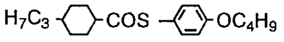
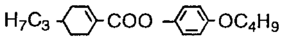
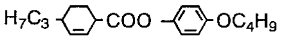
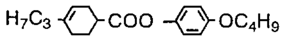
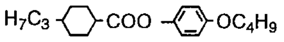
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm

Table 2. Mesomorphic properties of system (1) liquid crystals.

Compound No.	Structure	Phase behaviour/°C	Reference
1-1		Cr 73 N 119 I	[1, 2]
1-2		Cr 14 N 71 I	[1, 2]
1-3		Cr 54 N 105 I	[19]
1-4		Cr 79 N (76) I	[3]
1-5		Cr 24 N (0) I	[4]
1-6		Cr 51 N (49) I	[23]
1-7		Cr 57 N 74 I	[4]
1-8		Cr 36 N (32) I	[24]
1-9		Cr 81 Sm 102 N 125 I	[4]
1-10		Cr 64 N 109 I	[25]
1-11		Cr 22 N 59.5 I	[5]
1-12		Cr 49 N 53 I	[26]
1-13		Cr 44 I	[1]
1-14		Cr 21 N 46 I	[1]
1-15		Cr 8 I	[1]
1-16		Cr 41.5 N 72.5 I	[27]

their nematic–isotropic liquid phase transition temperatures ($T_{\text{N-I}}$) due to the overall polarizability being increased. However, only compound **1-1** shows higher values of $T_{\text{N-I}}$ and the crystal–nematic phase transition temperature ($T_{\text{C-N}}$) and a lower value of the nematic range ΔT; compound **1-2** exhibits lower values of the melting and clearing temperatures and a higher value of ΔT compared with those of the reference compound **1-3**. These findings can be expressed by the following orders of increase of the clearing temperatures T_{cl} (in this case $T_{\text{cl}} = T_{\text{N-I}}$) and the nematic ranges ΔT, depending on the type of molecular fragment A:

System (1)

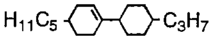
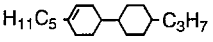
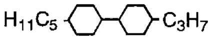
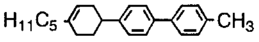
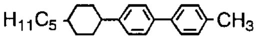
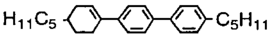
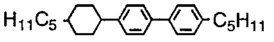
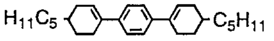
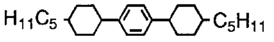
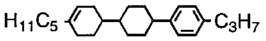
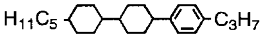
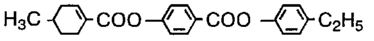
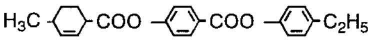
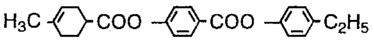
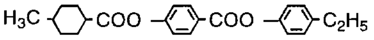
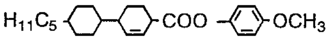
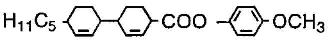
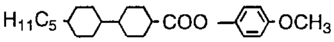
$T_{\text{cl}} \rightarrow$ A: Ceh2 < Ch < Ceh1; $\Delta T \rightarrow$ A: Ceh1 < Ch < Ceh2

where Ceh1 is the 1,4-cyclohex-1-enylene, Ceh2 is *trans*-1,4-cyclohex-2-enylene and Ch is the *trans*-1,4-cyclohexylene.

As can be seen from table 2, the introduction of the 1,4-cyclohex-1-enylene fragment in the molecular core of weakly polar two-ring alkyl-alkoxy derivatives results in the increase of their $T_{\text{C-N}}$ and $T_{\text{N-I}}$ values, while introducing the 1,4-cyclohex-3-enylene fragment in the same molecular core lowers their melting and clearing points compared with those of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives (compounds **1-4**–**1-6**, **1-7** and **1-8**).

The introduction of the CH=CH linking group in the molecular core of two-ring 1,4-disubstituted cyclohex-1-enylene and corresponding *trans*-1,4-disubstituted cyclohexylene derivatives does not change the orders of increase in the melting and clearing temperatures observed for compounds with the same molecular structure but without the above-mentioned linking group: 1,4-disubstituted cyclohex-1-enylene derivatives show higher clearing and melting temperatures than the corresponding *trans*-1,4-disubstituted cyclohexane

Table 3. Mesomorphic properties of system (2) liquid crystals.

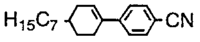
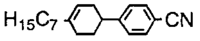
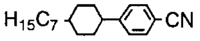
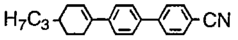
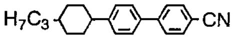
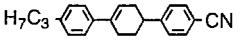
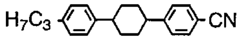
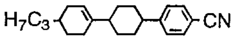
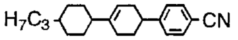
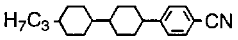
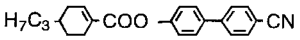
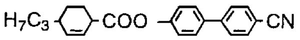
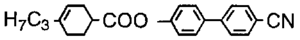
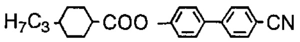
Compound No.	Structure	Phase behaviour/°C	Reference
2-1		Cr − 11 Sm 12 N 27 I	[6]
2-2		Cr − 10 Sm 19 N 22 I	[6]
2-3		Cr 31 Sm 97 I	[20]
2-4		Cr 53 Sm 114 N 132 I	[4]
2-5		Cr 98 Sm 123 N 178 I	[28]
2-6		Cr 101.5 SmB 180 SmA 194 I	[7]
2-7		Cr 13 SmB 164 N 166 I	[7]
2-8		Cr 91 Sm 144 N 167 I	[4]
2-9		Cr 50 Sm 196 I	[29]
2-10		Cr 82 N 113.6 I	[4]
2-11		Cr 48.6 Sm 181 I	[8]
2-12		Cr 96 N 169 I	[1]
2-13		Cr 53 N 162 I	[1]
2-14		Cr 58 N 165 I	[1]
2-15		Cr 85 N 193 I	[9]
2-16		Cr 42.5 N 154.5 I	[10]
2-17		Cr − 30 N 103 I	[10]
2-18		Cr 60 N 218 I	[10]

derivatives (compounds **1-4** and **1-6**, **1-9** and **1-10**). While introducing the COO linking group in the liquid crystalline molecular cores changes the order of increase in clearing temperatures, it leads to the disappearance of the mesophase and keeps the same order of increase in melting temperatures for the 1,4-disubstituted cyclohex-1-enylene derivatives (compounds **1-7** and **1-8**, **1-13** and **1-16**). Introduction of the COS linking group changes the order of increase in melting temperatures and keeps the same order of increase in clearing temperatures (compounds **1-7** and **1-8**, **1-11** and **1-12**).

It is clear from the data collated in table 2 that the replacement of the *trans*-1,4-cyclohexylene fragment by the *trans*-1,4-cyclohex-2-enylene and 1,4-cyclohex-3-enylene fragments to produce compounds **1-14** and **1-15** results in decreasing their melting and clearing points and the disappearance of the mesophase, respectively.

Compared with the smectic *trans*-1,4-disubstituted cyclohexylene derivative **2-3** presented in table 3, 1,4-disubstituted cyclohex-1-enylene derivative **2-1** and 1,4-disubstituted cyclohex-3-enylene derivative **2-2**, having increased molecular polarizability, exhibit significantly lower crystal–smectic phase transition temperatures; they also show smectic and nematic phases with greatly reduced thermal stabilities. The orders of increasing T_{cl} and ΔT are as follows:

Table 4. Mesomorphic properties of system (3) liquid crystals.

Compound No.	Structure	Phase behaviour/°C	Reference
3-1		Cr 47.5 N 61 I	[11]
3-2		Cr 35 N (5) I	[12]
3-3		Cr 30 N 59 I	[30]
3-4		Cr 71 I	[1]
3-5		Cr 17 N (9) I	[1]
3-6		Cr <20 I	[1]
3-7		Cr 52 N 70 I	[31]
3-8		Cr 110 N 232 I	[11]
3-9		Cr 133 N 230 I	[32]
3-10		Cr 114 N 172 I	[12]
3-11		Cr 123 N 160 I	[33]
3-12		Cr 68 N 183 I	[13]
3-13		Cr 62 N 167 I	[13]
3-14		Cr 72 N 242 I	[22]
3-15		Cr 109 N 224 I	[1]
3-16		Cr 59 N 203 I	[1]
3-17		Cr 63 N 172 I	[1]
3-18		Cr 94.3 N 248.6 I	[21]

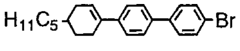
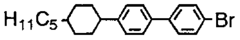
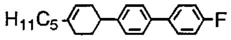
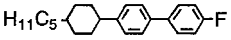
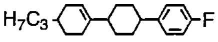
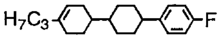
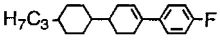
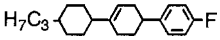
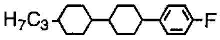
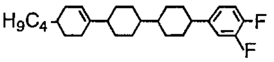
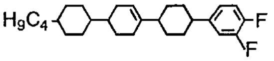
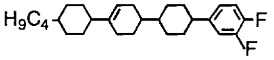
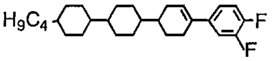
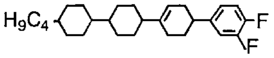
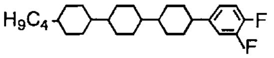
System (2)

$T_{cl} \rightarrow$ A: Ceh3 < Ceh1 < Ch; $\Delta T \rightarrow$ A: Ch < Ceh3 < Ceh1

where Ceh3 is the 1,4-cyclohex-3-enylene.

The thermal data presented in table 3 reveal that weakly polar three-ring 1,4-disubstituted cyclohex-3-enylene derivatives exhibit lower clearing points, and decreased thermal stability of the smectic phase or its disappearance; the corresponding 1,4-disubstituted cyclohex-1-enylene derivatives show higher melting and clearing points and disappearance of the nematic phase compared with those of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives (compounds **2-4** and **2-5**, **2-6** and **2-7**, **2-10** and **2-11**). It should be pointed out that the highly smectic character of the mesophases recorded for compound **2-6** makes it difficult to use as the component of liquid crystalline materials for nematic display applications. The melting points of the 1,4-disubstituted cyclohex-3-enylene derivatives show both increasing (compounds **2-10** and **2-11**) and decreasing (compounds **2-4** and **2-5**) values in comparison with those of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives. Interestingly, the replacement of two *trans*-1,4-cyclohexylene fragments by the 1,4-cyclohex-1-enylene fragment and 1,4-cyclohex-3-enylene fragment in compound **2-9** to produce compound **2-8** results in decreasing its clearing point, increasing its melting point and inducing the nematic phase.

Table 5. Mesomorphic properties of system (4) liquid crystals.

Compound No.	Structure	Phase behaviour/°C	Reference
4-1		Cr 165 N 235 I	[4]
4-2		Cr 153.4 N 192.7 I	[34]
4-3		Cr 68 N 107 I	[4]
4-4		Cr 100 N 153 I	[35]
4-5		Cr 56 N 97 I	[14]
4-6		Cr 76 N 95 I	[14]
4-7		Cr 59.7 N 150 I	[15]
4-8		Cr 45 N 91 I	[14]
4-9		Cr 90 N 158 I	[22]
4-10		Sm 148 N 241 I	[13]
4-11		Cr 60 Sm 160 N 244 I	[13]
4-12		Sm 158 N 235 I	[13]
4-13		Cr 87.1 Sm 174 N 245 I	[16]
4-14		Cr 64 Sm 170 N 238 I	[13]
4-15		Cr 72.2 Sm 217 N 299 I	[16]

As can be seen from table 3, weakly polar three-ring 1,4-disubstituted cylohexenyl derivatives with two incorporated COO linking groups exhibit only nematic phases; phase transition temperatures depend on the position of a double bond in their 1,4-cyclohexenylene fragment. *Trans*-1,4-disubstituted cyclohex-2-enylene and 1,4-disubstituted cyclohex-3-enylene derivatives exhibit lower melting points (compounds **2-13** and **2-14**) and 1,4-disubstituted cyclohex-1-enylene derivative (compound **2-12**) shows a higher melting point; all three 1,4-disubstituted cyclohexenylene derivatives show lower values of the clearing points compared with those of the reference compound **2-15**. These can be expressed by the following orders of increasing T_{cl} and ΔT:

System (3)

$$T_{cl} \rightarrow \text{A: Ceh2} < \text{Ceh3} < \text{Ceh1} < \text{Ch};$$

$$\Delta T \rightarrow \text{A: Ceh1} < \text{Ceh3} < \text{Ch} < \text{Ceh2}.$$

From table 3, it follows that by increasing the number of the *trans*-1,4-cyclohex-2-enylene fragments introduced into the molecular core of liquid crystals and, consequently increasing their molecular polariability, their clearing and melting points are decreased further (compounds **2-16**–**2-18**).

As in the case of weakly polar 1,4-disubstituted cyclohexenylene derivatives, strong polar two-ring cyano derivatives exhibit similar mesomorphic behaviour. The introduction of the 1,4-cyclohex-1-enylene fragment in their molecular cores increases the melting and clearing temperatures, and the introduction of the 1,4-cyclohex-3-enylene fragment lowers the clearing and increases the melting temperatures compared with those of the corresponding *trans*-1,4-disubstituted cyclohexylene derivative (compounds **3-1** and **3-3**, **3-2** and **3-3**, respectively; table 4).

The introduction of the COO linking group into the molecular cores of two-ring cyano derivatives incorporating 1,4-cyclohexenylene fragments, with different positions of their double bond, changes the order of increasing T_{cl} observed for two-ring 1,4-disubstituted cyclohex-1-enylene and the corresponding *trans*-1,4-disubstituted cyclohexylene cyano derivatives without the COO linking group. This results in a significant reduction of the melting and clearing points for the *trans*-1,4-disubstituted cyclohex-2-enylene derivative (compound **3-5**) and the disappearance of the mesophase for the 1,4-cyclohex-1-enylene and 1,4-cyclohex-3-enylene derivatives (compounds **3-4** and **3-6**, see also [1, 11]) in comparison with those of the reference compound **3-7**, table 4.

The data on phase transition temperatures presented in table 4 show that the effect on the mesomorphic behaviour of three-ring cyano derivatives strongly depends on their molecular structure. So far, the introduction of the 1,4-cyclohex-1-enylene or 1,4-cyclohex-3-enylene fragments in the molecular core of three-ring cyano derivatives incorporating two 1,4-phenylene fragments decreases their melting point and increases clearing temperature compared with those of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives (compounds **3-8** and **3-9**, **3-10** and **3-11**). The introduction of the above-mentioned fragments in the molecular core of three-ring cyano derivatives having two saturated *trans*-1,4-cyclohexylene fragments decreases both their melting and clearing temperatures compared with those of the reference liquid crystal (compounds **3-12**–**3-14**).

As in the case of two-ring cyano derivatives, the introduction of the COO linking group in the molecular cores of three-ring cyano derivatives changes the order of increase in clearing and melting temperatures observed for the 1,4-disubstituted cyclohex-1-enylene and corresponding *trans*-1,4-disubstituted derivatives without the COO linking group. This also results in decreasing the nematic–isotropic liquid phase transition temperature and increasing the crystal–nematic phase transition temperature of the 1,4-disubstituted cyclohex-1-enylene derivative compared with those of the reference liquid crystal (compounds **3-8** and **3-9**, **3-15** and **3-18**). The replacement of the *trans*-1,4-cyclohexylene fragment by the *trans*-1,4-cyclohex-2-enylene and 1,4-cyclohex-3-enylene fragments in compound **3-18** to produce compounds **3-16** and **3-17** lowers their melting and clearing points. These are consistent with the order of increasing the clearing temperatures and the nematic ranges for the system (4):

System (4)

$$T_{cl} \rightarrow \text{A: Ceh3} < \text{Ceh2} < \text{Ceh1} < \text{Ch};$$

$$\Delta T \rightarrow \text{A: Ceh3} < \text{Ceh1} < \text{Ceh2} < \text{Ch}.$$

These results reveal that the introduction of the 1,4-cyclohex-3-enylene fragment into the molecular core of system (4) compounds produces liquid crystals with the narrowest nematic phase and having the lowest thermal stability. However, introducing the 1,4-cyclohex-1-enylene and 1,4-cyclohex-2-enylene fragments gives liquid crystals with increased clearing temperatures or a broader nematic phase, respectively.

As can be seen from table 5, replacement of the *trans*-1,4-cyclohexylene fragment by the 1,4-cyclohex-1-enylene fragment in 4-bromo-4′-(*trans*-4-*n*-pentylcyclohexyl)biphenyl results in the increase of both its crystal–nematic and nematic–isotropic liquid transition temperatures, as compared with those of the corresponding reference liquid crystal (compounds **4-1** and **4-2**). The high melting point (165°C) observed for compound **4-1** makes it difficult to use as a component of liquid crystalline materials for nematic display applications. However, the replacement of the *trans*-1,4-cyclohexylene fragment by the 1,4-cyclohex-3-enylene fragment in 4-fluoro-4′-(*trans*-4-*n*-pentylcyclohexyl)biphenyl and 1-[*trans*-4-(*trans*-4-*n*-propylcyclohexyl)cyclohexyl]-4-fluorobenzene, or by the 1,4-cyclohex-1-enylene fragment in the latter compound, leads to the decrease in melting and clearing temperatures, as compared with those of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives (compounds **4-3** and **4-4**, **4-5**–**4-9**), see also [17, 18]. These can be expressed by the following orders of increasing T_{cl} and ΔT:

System (5)

$$T_{cl} \rightarrow \text{A: Ceh3} < \text{Ceh1} < \text{Ch}; \ \Delta T \rightarrow \text{A: Ceh3} < \text{Ceh1} < \text{Ch}$$

System (6)

$$T_{cl} \rightarrow \text{A: Ceh3} < \text{Ceh1} < \text{Ch}; \ \Delta T \rightarrow \text{A: Ceh3} < \text{Ch} < \text{Ceh1}.$$

These indicate that the introduction of the 1,4-cyclohex-3-enylene fragment into the molecular core of systems (5) and (6) compounds produces liquid crystals with the narrowest nematic phase and having the lowest thermal stability. The order of increase in the clearing temperatures is the same for any of two positions on introduction of the 1,4-cyclohex-1-enylene and 1,4-cyclohex-3-enylene fragments into the molecular core of the liquid crystals belonging to these systems.

Interestingly, on moving the position of the 1,4-cyclohex-3-enylene fragment from the alkyl group to a position close to the 1,4-phenylene fragment there is a decrease in both melting and clearing points (compounds **4-6** and **4-8**). The same movement of the position of the 1,4-cyclohex-1-enylene fragment increase the melting and clearing points (compounds **4-5** and **4–7**).

The influence of the introduction of the 1,4-cyclohexenylene fragment into three-ring fluoro derivatives can be expressed by the following orders of increase in clearing temperatures and nematic ranges:

System (7)

$T_{\rm cl}\rightarrow$ A-B: Ch-Ceh3 < Ceh3-Ch < Ceh1-Ch
< Ch-Ch1 < Ch-Ch;
$\Delta T\rightarrow$ A-B: Ceh3-Ch < Ceh1-Ch < Ch-Ceh3
< Ch-Ch < Ch-Ch1.

These results reveal that the introduction of the 1,4-cyclohex-1-enylene fragment as the central ring B in the molecular core of system (7) is the most favourable for achieving the broadest nematic phase with moderate thermostability.

Comparison of the thermal data for the four-ring difluoro derivatives presented in table 5 shows that the smectic–nematic and nematic–isotropic liquid transition temperatures are lower for 1,4-disubstituted cyclohexenylene derivatives than for the corresponding *trans*-1,4-cyclohexylene derivative (compounds **4-10–4-15**). Hence, for the liquid crystals investigated, the orders of increasing $T_{\rm cl}$ and ΔT are as follows:

System (8)

$T_{\rm cl}\rightarrow$ A: Ceh3 < Ceh1 < Ch; $\Delta T\rightarrow$ A: Ceh3 < Ch < Ceh1

System (9)

$T_{\rm cl}\rightarrow$ A: Ceh3 < Ceh1 < Ch; $\Delta T\rightarrow$ A: Ceh3 < Ch1 < Ch.

These results indicate that the introduction of the 1,4-cyclohex-3-enylene fragment into the molecular core of systems (8) and (9) compounds produces liquid crystals with the narrowest nematic phase and having the lowest thermal stability. The order of increase in clearing temperatures is the same for any of two positions on introduction of the 1,4-cyclohex-1-enylene and 1,4-cyclohex-3-enylene fragments into the molecular core of the liquid crystals belonging to these systems.

The compounds of systems (8) and (9) as well as of (5) and (6) show the same order of increase in clearing points despite the increasing alkyl chain length, the introduction of the additional *trans*-1,4-cyclohexylene fragment into the molecular core and the lateral fluoro substitution of the 1,4-phenylene fragment in systems (8) and (9), as compared with those of systems (5) and (6).

As can be seen from table 5, movement of the position of the 1,4-cyclohex-1-enylene fragment from the alkyl group to a position close to the 1,4-phenylene fragment increases both the smectic–nematic and nematic–isotropic liquid phase transition temperatures (compounds **4-10**, **4-11**, **4-13**). The same movement of position of the 1,4-cyclohex-3-enylene fragment also increases these phase transition temperatures (compounds **4-12**, **4-14**); this is the opposite situation to the results seen above for three-ring 1,4-disubstituted cyclohex-3-enylene fluoro derivatives. The introduction of the 1,4-cyclohexenylene fragment into the molecular core of four-ring difluoro derivatives leads to the following orders of increase in clearing temperatures and the nematic ranges:

System (10)

$T_{\rm cl}\rightarrow$ A-B-K: Ch-Ceh3-Ch < Ch-Ch-Ceh3 < Ceh1-Ch-Ch
< Ch-Ceh1-Ch < Ch-Ch-Ceh1 < Ch-Ch-Ch;
$\Delta T\rightarrow$ A-B-K: Ch-Ch-Ceh3 < Ch-Ch-Ceh1 < Ch-Ceh3-Ch
< Ch-Ch-Ch < Ch-Ceh1-Ch < Ceh1-Ch-Ch.

These results reveal that the introduction of the 1,4-cyclohex-3-enylene fragment into the molecular core of system (10) compounds gives liquid crystals with lowest clearing temperatures; the similar introduction of the 1,4-cyclohex-1-enylene fragment, particularly as the ring K, increases the nematic–isotropic phase transition temperatures. In the case of the nematic range, introduction of the 1,4-cyclohex-3-enylene fragment into system (10) compounds as the ring K results in the narrowest nematic range, while introduction of the 1,4-cyclohex-1-enylene fragment as the ring A gives the broadest nematic range.

The results presented together with ref. [12] show that the mesomorphic behaviour of 1,4-disubstituted cyclohexenylene derivatives is difficult to predict using a rationalization in terms of only anisotropy of polarizability and based on the Maier–Saupe theory [36]. It has been suggested that the packing of the molecules predominantly influences the thermodynamical stability of the nematic phase [12]. Other molecular aspects, such as association [37, 38] or dipole–dipole attraction in polar liquid crystals, which can influence the packing of the molecules will also affect the stability of the nematic phase [12].

3. Static dielectric, optical, elastic and electro-optical properties

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ (where $\varepsilon_\parallel$ 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 [39]:

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

where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$; $\Delta\alpha = (a_\parallel - \alpha_\perp)$, 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; S is the order parameter.

It has been shown that 1,4-disubstituted cyclohexenylene derivatives having higher values of polarizability exhibit higher values of dielectric anisotropy compared with those of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives; this is in agreement with equation (1), see compounds **5-1** and **5-2**, **5-3**–**5-6**, table 6.

The phenomenological relation between refractive index and electric polarization is defined as [43, 44]:

$$(n^{*2} - 1)/(n^{*2} + 2) = N\alpha^*/3\varepsilon_0 \qquad (2)$$

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 index. From equation (2) and the previous discussion, it follows that the 1,4-disubstituted cyclohexenylene derivatives which have large induced polarizability of their π-electron system exhibit an optical anisotropy $\Delta n = n_e - n_o$ that is larger than that of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives (compounds **5-1** and **5-2**).

The elastic constant ratio K_{33}/K_{11} of liquid crystalline materials is a parameter of great importance for super twisted nematic-liquid crystal displays (STN-LCDs), defining their electro-optical performance [45]. It has been found that the position of a double bond in the 1,4-cyclohexenylene fragment and its position in the molecular core of nematic liquid crystals have a strong effect on their elastic constants (compounds **5-3**, **5-5**, **5-6**, table 6). Compound **5-3**, having an alkyl chain attached to the 1,4-cyclohex-1-enylene fragment, shows a lower value of the elastic constant K_{11} and a higher value of the elastic constant ratio K_{33}/K_{11} compared with those of compound **5-5** (having the 1,4-cyclohex-3-enylene fragment attached to the 3′,4′-difluorophenylene fragment) and the reference liquid crystal **5-6** (only K_{33}/K_{11}).

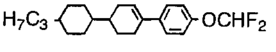
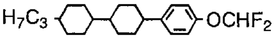
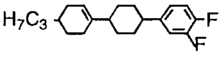
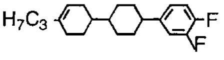
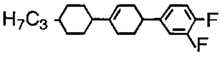
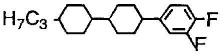
It has been demonstrated that the threshold voltage of the twist-effect can be expressed as follows [46]:

$$V_{\mathrm{th}} \propto \pi[\kappa/\varepsilon_0\Delta\varepsilon]^{1/2} \qquad (3)$$

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

As can be seen from table 6 compounds **5-3** and **5-5**, having approximately equal values of the dielectric

Table 6. Dielectric, optical, elastic and electro-optical properties of system (5) liquid crystals.

Compound No.	Structure	$T_{\mathrm{N\text{-}I}}$/°C	$\Delta\varepsilon$	Δn	$K_{11} \times 10^{-12}$/N	$\frac{K_{33}}{K_{11}}$	Vth/V	Ref.
5-1		167.7	3.6[a]	0.154[b]				[40]
5-2		173.6	3.2[a]	0.114[b]				[40]
5-3		59	5.6[c]	0.078[c]	6.1[c]	3.1[c]	1.62[c]	[14, 41]
5-4		53	5.0[d]	0.073[d]				[14, 41]
5-5		55	5.6[e]	0.075[e]	7.9[e]	1.8[e]	1.76[e]	[14, 41]
5-6		123.8	3.2[f]			1.9[g]	1.8[f]	[42]

[a] $\tau = T/T_{\mathrm{N\text{-}I}} = 0.85$; T/K, $T_{\mathrm{N\text{-}I}}$/K.

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

[c] $T_{\mathrm{meas}} = T_{\mathrm{N\text{-}I}} - 34$°C.

[d] $T_{\mathrm{meas}} = T_{\mathrm{N\text{-}I}} - 28$°C.

[e] $T_{\mathrm{meas}} = T_{\mathrm{N\text{-}I}} - 30$°C.

[f] $T_{\mathrm{meas}} = T_{\mathrm{N\text{-}I}} - 35$°C.

[g] $T_{\mathrm{meas}} = T_{\mathrm{N\text{-}I}} - 58$°C.

Table 7. Viscosity and electro-optical parameters of the liquid crystalline mixtures [1][a]: cell gap $d = 10\,\mu$m, $T_{\mathrm{meas}} = 20$°C.

Compound	**2-12**	**2-13**	**2-14**	**2-15**
$T_{\mathrm{N\text{-}I}}$/°C	67.8	66.3	67.1	73.9
Threshold voltage/V	1.34	1.36	1.30	1.49
Saturation voltage/V	1.86	1.85	1.82	1.96
Switch-on time/ms	80	70	75	55
Switch-off time/ms	150	150	150	140
Viscosity/mm^2 s^{-1}	49	42	48	38.5

[a] The mixtures are composed of 75 wt % of 4-*n*-pentyl-4′-cyanobiphenyl and 25 wt % of one of the compounds 2-12, 2-13, 2-14, 2-15, respectively.

anisotropy, differ in the value of elastic constant K_{11} which, according to equation (3), has a proportional influence on the threshold voltage of the twist-effect. That is, the increased value of K_{11} corresponds to the increased value of V_{th} for compound **5-5**.

Table 7 presents the viscosity and electro-optical parameters of liquid crystalline mixtures composed of 4-*n*-pentyl-4′-cyanobiphenyl and one of the 1,4-disubstituted cyclohexenylene and *trans*-1,4-disubstituted cyclohexylene derivatives. It can be seen that liquid crystalline mixtures containing 1,4-disubstituted cyclohexenylene derivatives exhibit higher values of the kinematic viscosity and lower values of the threshold and saturation voltages of the twist-effect compared with those of the mixture containing the corresponding *trans*-1,4-cyclohexylene derivative. These results can be used for the development of liquid crystalline materials for nematic display applications with decreased power consumption.

4. Conclusion

Systematic studies on the effects of structure–property relationships in liquid crystalline 1,4-disubstituted cyclohexenylene derivatives have been performed, with attempts to correlate the molecular level parameters with the observed mesomorphic and physical properties. The information here presented may lead to a better understanding of the nature of liquid crystals and their use for nematic display applications.

References

[1] Bezborodov, V. S., Konovalov, V. A., Lapanik, V. I., and Minko, A. A., 1989, *Liq. Cryst.*, **4,** 209.

[2] Bezborodov, V. S., Konovalov, V. A., Lapanik, V. I., and Minko, A. A., 1988, *Z. org. Khim.*, **24,** 615.

[3] Bezborodov, V. S., Dabrowski, R., and Dziaduszek, J., 1995, *Proc. SPIE*, **2372,** 242.

[4] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., and Petrov, V. F., 1997, *Liq. Cryst.*, **23,** 69.

[5] Sato, H., Takatsu, H., and Tazume, M., 1978, German Patent Application DE 2847639.

[6] Tanaka, Y., Takatsu, H., and Takeuchi, H., 1986, EU Patent Application EP 0198714.

[7] Hird, M., and Toyne, K. J., 1995, *J. mater. Chem.*, **5,** 2239.

[8] Sugimori, S., Kojima, T., and Tsuji, 1982, EU Patent Application EP 62470.

[9] Bezborodov, V. S., Lapanik, V. I., and Grinkevich, O. A., 1987, *Z. org. Khim.*, **23,** 150.

[10] Vill, V., 1994, *Liquid Crystals*, edited by J. Thiem, Landolt-Bornstein, IV/7d (New York: Springer Verlag), pp. 360, 362, 368.

[11] Inukai, T., Inoue, H., and Sato, H., 1980, US Patent 4211666.

[12] Osman, M. A., and Revesz, L., 1982, *Mol. Cryst. liq. Cryst.*, **82,** 41.

[13] Tanaka, Y., Takatsu, H., Takeuchi, K., and Tamura, Y., 1994, US Patent 5321169.

[14] Tanaka, Y., Takatsu, H., Takeuchi, K., and Tamura, Y., 1989, EU Patent Application EP 310067.

[15] Sugimori, S., Kojima, T., and Tsuji, M., 1982, German Patent Application DE 3739130.

[16] Sugimori, S., and Kojima, T., 1984, US Patent 4472293.

[17] Uchida, M., and Goto, Y., 1991, EU Patent Application EP 410756.

[18] Matsui, S., Goto, Y., Onji, Y., and Fujita, A., 1993, EU Patent Application EP 568040.

[19] Schubert, H., Dehne, R., and Uhlig, V., 1972, *Z. Chem.*, **12,** 219.

[20] Kelly, S. M., 1994, *Liq. Cryst.*, **17,** 211.

[21] Gray, G. W., and McDonnell, D. G., 1979, *Mol. Cryst. liq. Cryst.*, **53,** 147.

[22] Plach, H., Bartmann, E., Poetsch, E., Naemura, S., and Rieger, B., 1992, *SID 92 Digest*, p. 13.

[23] Schadt, M., Buchecker, R., Leenhouts, F., Boller, A., Villiger, A., and Petrzilka, M., 1986, *Mol. Cryst. liq. Cryst.*, **139,** 1.

[24] Merck Liquid Crystals, 1986, product information.

[25] Takatsu, H., Takeuchi, K., and Sato, H., 1983, *Mol. Cryst. liq. Cryst.*, **94,** 255.

[26] Sato, H., Takatsu, H., Tazume, M., and Fujita, Y., 1979, German Patent Application DE 2905992.

[27] Deutcher, H. J., Laaser, B., Dolling, W., and Schubert, H., 1978, *J. prakt. Chem.*, **320,** 191.

[28] Eidenschink, R., and Romer, M., 1983, in Proceedings of the 13th Freiburger Arbeitstagung Flussigkristalle, V. 4.

[29] Eidenschink, R., Pohl, L., Romer, M., and del Pino, F., 1981, EU Patent Application EP 030277.

[30] Eidenschink, R., Erdmann, D., Krause, J., and Pohl, L., 1977, *Angew. Chem.*, **89,** 103.

[31] Takahashi, M., Mita, S., and Kondo, S., 1986, *Mol. Cryst. liq. Cryst.*, **132,** 53.

[32] Chandrasekhar, S., 1980, *Liquid Crystals* (Cambridge: Cambridge University Press), p. 515.

[33] Eidenschink, R., Krause, J., and Pohl, L., 1978, German Patent Application DE 2701591.

[34] Muller, H. J., and Haase, W., 1983, *Mol. Cryst. liq. Cryst.*, **92,** 63.

[35] Eidenschink, R., 1983, *Mol. Cryst. liq. Cryst.*, **94,** 119.

[36] Maier, W., and Saupe, A., 1959, *Z. Naturforsch.*, **14a,** 882.

[37] Schad, Hp., and Osman, M. A., 1981, *J. chem. Phys.*, **75,** 880.

[38] Grebyonkin, M. F., Petrov, V. F., and Ostrovsky, B. I., 1990, *Liq. Cryst.*, **7**, 367.

[39] Maier, W., and Meier, G., 1961, *Z. Naturforsch.*, **16a,** 262.

[40] Pavluchenko, A. I., Smirnova, N. I., Petrov, V. F., Fialkov, Y. A., Shelyazhenko, S. V., and Yagupolski, L. M., 1991, *Mol. Cryst. liq. Cryst.*, **209,** 225.

[41] DIC's Recent Liquid Crystal Materials, September 30, 1988, product information.

[42] Demus, D., Goto, Y., Sawada, S., Nakayama, E., Saito, H., and Tarao, R., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 1.

[43] De Jeu, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach).

[44] De Jeu, W. H., Gerritsma, C. J., van Zenten, P., and Goosens, W. A., 1972, *Phys. Lett. A*., **39,** 355.

[45] Guy, S. C., 1993, *Displays*, **13,** 32.

[46] Schadt, M., 1992, *Displays*, **13,** 11.