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# Liquid Crystals

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# The *trans*-1,4-cyclohexylene group as a structural fragment in liquid crystals

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In this review the effect on physico-chemical and electro-optical properties of the introduction of the *trans*-1,4-cyclohexylene fragment into the molecular core of liquid crystals is discussed, rationalized in terms of existent theories, and compared with the effect of other well-known molecular fragments.

## 1. Introduction

The rapid development of liquid crystal display (LCD) technology is closely connected with the progress made in liquid crystal materials research. It has been shown that one of the important prerequisites for the development of liquid crystalline materials for display applications is the definition of the structure–property relationships for the liquid crystals [1–5]. In continuation of our work (see, for example [5–10]), the effect of introducing the *trans*-1,4-cyclohexylene fragment into the molecular core of liquid crystals for nematic display applications will be reviewed, rationalized in terms of existent theories, and compared with the effect of other well-known molecular fragments.

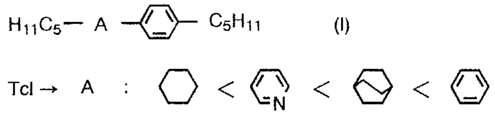
In order to avoid additional effects on molecular polarizability and flexibility [11, 12] and on the efficiency of molecular fragments [6, 8, 9], we decided to study laterally unsubstituted liquid crystalline derivatives having only single carbon–carbon bonds between their rings.

## 2. Mesomorphic properties

### 2.1. *Thermal and general data*

Many attempts have been made to understand the factors such as rigidity, linearity, size and polarizability of molecular fragments influencing mesophase stability [1, 2, 4, 13–15]. However, the prediction and rationalization of mesomorphic properties of liquid crystals still remain difficult problems [2, 4, 16–18]. The purpose of this section is therefore to define what relations can be established for liquid crystals incorporating the *trans*-1,4-cyclohexylene fragment in their molecular cores, even though these relationships may be empirical.

The effect of introducing the *trans*-1,4-cyclohexylene fragment in the molecular core of liquid crystals on their mesomorphic properties is shown in tables 1–12. As can be seen from table 1, the weakly polar two-ring dialkyl phenylcyclohexane derivative exhibits monotropic smectic–nematic ($T_{\mathrm{Sm\text{-}N}}$) and nematic–isotropic ($T_{\mathrm{N\text{-}I}}$) phase transitions (compound **1-1**). Replacing the *trans*-1,4-cyclohexylene fragment in compound **1-1** by the 1,4-phenylene or pyridin-2,5-diyl or 1,4-bicyclo[2.2.2]-octylene fragments, to give compounds **1-2**, **1-3**, **1-4**, respectively, significantly increases their melting and clearing points. It is useful to express the effect of introducing the *trans*-1,4-cyclohexylene fragment on the mesomorphic behaviour of liquid crystals, and compare with that for other well-known liquid crystalline derivatives, by the following order of increasing clearing temperatures ($T_{\mathrm{Cl}}$) depending on the type of molecular fragment *A* for the system (I):



(I)

The low nematic thermostability of compound **1-1** is explained in terms of low density packing of its molecules compared with that of the corresponding compounds **1-2** and **1-5** [19]. The replacement of the 1,4-phenylene fragment in compound **1-1** by the *trans*-1,4-cyclohexylene fragment to give compound **1-5** increases the melting and clearing temperatures and creates a smectic phase with a greater thermostability than that observed

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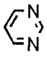
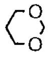
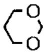
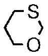
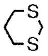
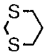
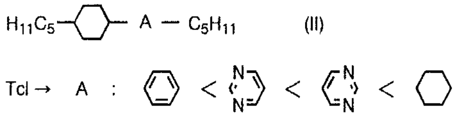
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm

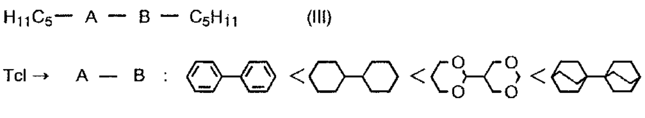
Table 1. Mesomorphic properties of some liquid crystals: $H_{11}C_5$–A–B–$(O)_nC_mH_{2m+1}$.

| Compound | A | B | *n* | *m* | Phase transitions/°C | Ref. |
|---|---|---|---|---|---|---|
| **1-1** |  |  | 0 | 5 | Cr – 0.8 Sm (– 8) N (– 5) I | [19] |
| **1-2** |  |  | 0 | 5 | Cr 26 SmE 47.6 SmB 52.2 I | [19] |
| **1-3** |  |  | 0 | 5 | Cr 33 Sm (32) I | [20] |
| **1-4** |  |  | 0 | 5 | Cr 52 N (33) I | [21] |
| **1-3** |  |  | 0 | 5 | Cr 40 Sm 110.4 I | [22] |
| **1-6** |  |  | 0 | 5 | Cr 33.5 Sm 60 I | [23] |
| **1-7** |  |  | 0 | 5 | Cr 17 N (10) I | [23] |
| **1-8** |  |  | 0 | 5 | Cr 42 SmB 246 I | [24] |
| **1-9** |  |  | 0 | 5 | Cr 92.8 SmB 134 I | [25] |
| **1-10** |  |  | 1 | 2 | Cr 51 N (49) I | [26] |
| **1-11** |  |  | 1 | 2 | Cr 72 S 81 I | [27] |
| **1-12** |  |  | 1 | 2 | Cr 60.5 N 62 I | [20] |
| **1-13** |  |  | 1 | 2 | Cr 73 N 86 I | [21] |
| **1-14** |  |  | 1 | 2 | Cr 85 I | [28] |
| **1-15** |  |  | 1 | 2 | Cr 57 I | [29] |
| **1-16** |  |  | 1 | 2 | Cr 55 I | [29] |
| **1-17** |  |  | 1 | 2 | Cr 35 SmB 56 N 63 I | [30] |

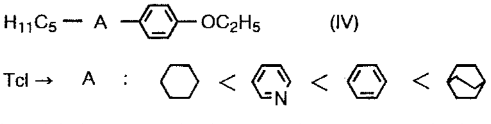
for their biphenyl analogue **1-2**. Replacing the *trans*-4-pentylcyclohexyl fragment in compound **1-5** by the pentylpyrimidine fragment to produce compounds **1-6** and **1-7** lowers their melting and clearing points:



The replacement of two *trans*-1,4-cyclohexylene fragments by two 1,4-bicyclo[2.2.2]octylene or *trans*-1,3-dioxan fragments in compound **1-5** to give compounds **1-8** and **1-9**, respectively, increases the clearing temperatures and maintains the highly smectic character of their phases:

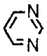
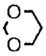
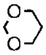


As can be seen from table 1, the two-ring alkylalkoxy *trans*-1,4-disubstituted cyclohexylene derivative exhibits the lowest nematic thermostability among the compounds, **1-10**–**1-13**.



It should be noted that replacement of the *trans*-1,4-cyclohexylene fragment in compound **1-10** by sulphur-containing fragments, to give the compounds **1-14**–**1-16** causes the disappearance of the mesophase. Replacing the 1,4-phenylene fragment by the *trans*-1,4-cyclohexylene fragment in the molecular core of compound **1-10**, to create the compound **1-17**, results in increased nematic thermostability and introduction of the smectic phase, while their biphenyl analogue **1-11** remains the compound with highest thermostability. This is opposite

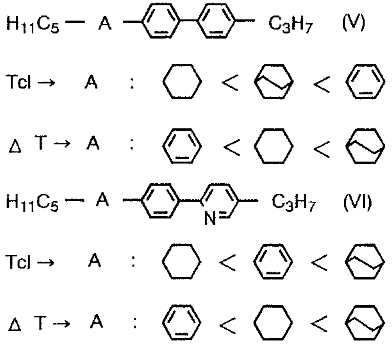
Table 2. Mesomorphic properties of some liquid crystals: $H_{11}C_5$–A–B–K–$C_3H_7$.

| Compound | A | B | K | Phase transitions/°C | Ref. |
|---|---|---|---|---|---|
| **2-1** |  |  |  | Cr 29 Sm 160 N 170 I | [31] |
| **2-2** |  |  |  | Cr 180 SmE 200 SmB 214 SmA 218 I | [32] |
| **2-3** |  |  |  | Cr 175 SmB 191 N 210 I | [21] |
| **2-4** |  |  |  | Cr 48.6 Sm 181 I | [33] |
| **2-5** |  |  |  | Cr 48 SmB 163 SmA 184 N 185 I | [34] |
| **2-6** |  |  |  | Cr 58 SmB 124 SmA 134 N 156 I | [34] |
| **2-7** |  |  |  | Cr 51 Sm 190 I | [23] |
| **2-8** |  |  |  | Cr 41 Sm 156 N 160 I | [31] |
| **2-9** |  |  |  | Cr 101 N 187 I | [35] |
| **2-10** |  |  |  | $Cr_2$ 45.3 $Cr_1$ 72.4 N 157.3 I | [36] |
| **2-11** |  |  |  | Cr 37 Sm 93.5 N 179 I | [37] |
| **2-12** |  |  |  | $Cr_2$ 113 $Cr_1$ 154 SmB 181 SmA 195 N 201 I | [38] |
| **2-13** |  |  |  | Cr< 15 SmB 157 I | [34] |
| **2-14** |  |  |  | Cr 86 Sm 91 SmB 164 SmA 201 N 203 I | [34] |
| **2-15** |  |  |  | Cr 171 N 198 I | [34] |
| **2-16** |  |  |  | Cr 113 Sm 121 N 225 I | [7] |
| **2-17** |  |  |  | Cr 85.4 Sm (80.5) SmB 86.2 N 162.9 I | [36] |
| **2-18** |  |  |  | Cr 77.8 Sm 196.4 N 198.6 I | [39] |

to the mesomorphic behaviour observed for compounds **1-1**, **1-2** and **1-5**.

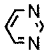
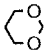
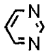
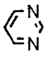
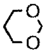
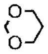
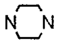
These results, and the different orderings obtained for the systems (I) and (IV), reveal that the influence on mesomorphic properties of the *trans*-1,4-cyclohexylene fragment depends also on the types of terminal substituents.

As in the case of two-ring weakly polar dialkyl *trans*-1,4-disubstituted cyclohexylene derivatives, the three-ring weakly-polar 4-propyl-4′-(*trans*-4-pentylcyclohexyl)-biphenyl and 5-propyl-2-[4-(*trans*-4-pentylcyclohexyl)-phenyl]pyridine exhibit lower clearing and melting points than those of the corresponding derivatives incorporating the biphenyl and phenylpyridine fragments, respectively, (compounds **2-1**–**2-3**; **2-11**, **2-15**, **2-16**; table 2):

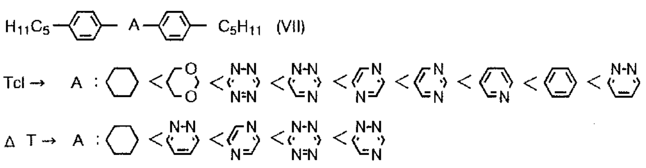


where Δ*T* is the nematic range.

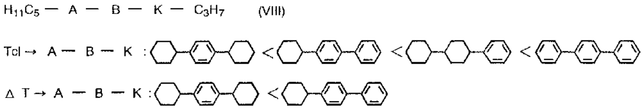
Table 3. Mesomorphic properties of some liquid crystals: $H_{11}C_5$–A–B–K–$C_5H_{11}$.

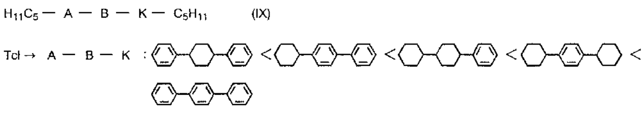
| Compound | A | B | K | Phase transitions/°C | Ref. |
|---|---|---|---|---|---|
| **3-1** |  |  |  | Cr 13 Sm 164 N 170 I | [40] |
| **3-2** |  |  |  | Cr< 30 Sm 189.8 I | [33] |
| **3-3** |  |  |  | Cr 50 Sm 196 I | [41] |
| **3-4** |  |  |  | Cr 80 Sm 112.7 I | [42] |
| **3-5** |  |  |  | Cr 192 Sm 213 I | [43] |
| **3-6** |  |  |  | Cr 99 Sm 205 I | [44] |
| **3-7** |  |  |  | Cr 106 SmA 195 I | [45] |
| **3-8** |  |  |  | Cr 84.5 Sm 140 I | [46] |
| **3-9** |  |  |  | Cr 134.3 SmC 173.6 SmA 182.2 N 191.3 I | [47] |
| **3-10** |  |  |  | Cr 195 Sm 219 N 224 I | [48] |
| **3-11** |  |  |  | Cr 150 SmC 169 N 185 I | [49] |
| **3-12** |  |  |  | Cr 163 N 172.5 I | [50] |
| **3-13** |  |  |  | Cr 171.8 Sm 213.4 I | [51] |
| **3-14** |  |  |  | Cr 179 N 189.5 I | [52] |
| **3-15** |  |  |  | Cr 156 N 165 I | [46] |
| **3-16** |  |  |  | Cr 50 SmB 155.9 I | [53] |

These results reveal that the effect of the *trans*-1,4-cyclohexylene fragment in systems (V) and (VI) depends on their structures. The introduction of the *trans*-1,4-cyclohexylene fragment as a middle ring in the molecular core of system (VII) gives liquid crystals exhibiting only a low melting smectic phase with the lowest thermostability among compounds **3-4**–**3-12**:



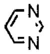
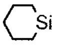
The effect of introducing *trans*-1,4-cyclohexylene fragments, their quantity and positions in the molecular cores of liquid crystals, is presented in tables 2 and 3, and can be expressed as follows (compounds **2-1**, **2-2**, **2-4**, **2-8**; **3-1**–**3-5**):





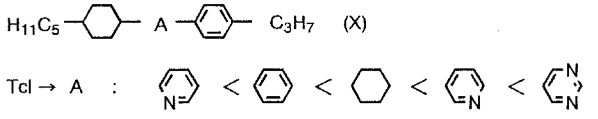
These results show that 1-(*trans*-4-propylcyclohexyl)-4-(*trans*-4-pentylcyclohexyl)-benzene exhibits the lowest clearing point, while 1-[*trans*-4-pentylcyclohexyl)-cyclohexyl]-4-propylbenzene shows moderate thermostability of its only smectic phase among system (VIII) compounds. Increasing the alkyl chain length results in

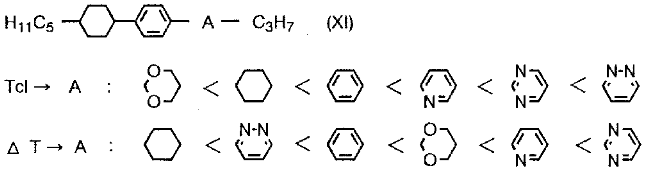
Table 4. Mesomorphic properties of liquid crystals: $H_{2n+1}C_n$–A–B–K–L–X.

| Compound | *n* | A | B | K | L | X | Phase transitions/°C | Ref. |
|---|---|---|---|---|---|---|---|---|
| **4-1** | 5 |  |  |  |  | $C_3H_7$ | Cr 58 SmB 232 SmA 251 N 311 I | [54] |
| **4-2** | 5 |  |  |  |  | $C_3H_7$ | Cr 55 Sm 255 N 312 I | [55] |
| **4-3** | 5 |  |  |  |  | $C_3H_7$ | Cr 119.4 Sm 186.5 N 323 I | [56] |
| **4-4** | 5 |  |  |  |  | $C_3H_7$ | Cr 20 Sm 165.5 N 172 I | [57] |
| **4-5** | 5 |  |  |  |  | $C_3H_7$ | Sm 197.9 N 252.2 I | [58] |
| **4-6** | 5 |  |  |  |  | $C_3H_7$ | Sm 191.9 N 231.9 I | [58] |
| **4-7** | 5 |  |  |  |  | $C_5H_{11}$ | Cr 297 SmA 352 I | [59] |
| **4-8** | 5 |  |  |  |  | $C_5H_{11}$ | Cr 55 Sm 247 SmA 275 N 305 I | [54] |
| **4-9** | 5 |  |  |  |  | $C_5H_{11}$ | Cr< 30 Sm > 300 I | [60] |
| **4-10** | 5 |  |  |  |  | $C_5H_{11}$ | Cr 20 SmA 30 N 73 I | [57] |
| **4-11** | 3 |  |  |  |  | F | Cr 140 SmA 147 N 301 I | [61] |
| **4-12** | 3 |  |  |  |  | F | Sm 190 N> 300 I | [60] |
| **4-13** | 3 |  |  |  |  | F | Cr 105.9 Sm 238 N 279 I | [62] |
| **4-14** | 3 |  |  |  |  | F | Cr 149.1 Sm 175.8 N 249.8 I | [63] |

changing the order of increasing $T_{cl}$ [systems (VIII) and (IX)], showing that terminal groups can modify the effect of introduced *trans*-1,4-cyclohexylene fragments into the molecular core.

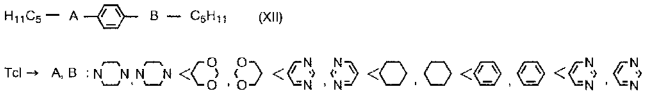
The effect on mesomorphic properties of replacing of one of two *trans*-1,4-cyclohexylene fragments by other molecular fragments is well illustrated by comparing the phase transition temperatures of the compounds presented in table 2 (compounds **2-1**, **2-4**–**2-7**; **2-1**, **2-8**–**2-12**):





The different results obtained for systems (X) and (XI) show that the effect on mesomorphic properties of introducing the depends on the position of the *trans*-1,4-cyclohexylene fragment in their cores.

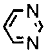
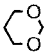
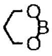
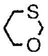
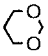
The effect of replacing two *trans*-1,4-cyclohexylene fragments by other fragments in compound **3-3** (which exhibits only a smectic phase with moderate thermostability), to give the compounds **3-5**, **3-13**–**3-16** (table 3), is demonstrated by system (XII):



Interestingly, the replacement of two 1,4-phenylene fragments by two *trans*-1,4-cyclohexylene fragments in compounds **2-2**; **2-14**; **3-5** and **2-17** to give compounds **2-4**, **2-8**; **2-13**; **3-2**, **3-3** and **2-18**, results in decreasing and increasing clearing points, respectively.

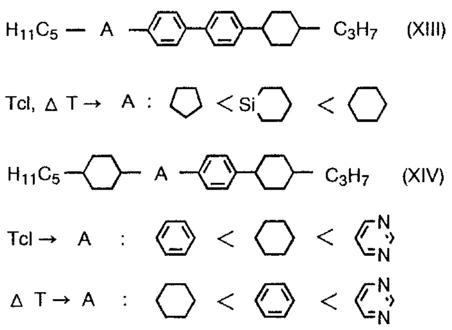
The effect on mesomorphic properties of introducing the *trans*-1,4-cyclohexylene fragment into the molecular core of four-ring weakly polar dialkyl derivatives is revealed by considering the thermal data recorded in table 4 for compounds **4-1**–**4-6**; **4-7**–**4-10**, and can be

Table 5. Physico-chemical properties of some liquid crystals: $H_{11}C_5$–A–B–CN.

| Compound | A | B | Phase transitions/°C | $d_1$/Å | $d_2$/Å | $\zeta_1$/Å | $\zeta_2$/Å | Ref. |
|---|---|---|---|---|---|---|---|---|
| **5-1** |  |  | Cr 31 N 55 I | | 25.9[a] | | 54[a] | [64, 65] |
| **5-2** |  |  | Cr 22.5 N 35 I | 14.3[a] | 24.8[a] | 38[a] | 58[a] | [65, 66] |
| **5-3** |  |  | Cr 33.6 N 43.5 I | 15.4[a] | 22.7[a] | 42[a] | 52[a] | [65, 67] |
| **5-4** |  |  | Cr 62 N 100 I | | 25.9[a] | | 47[a] | [65, 68] |
| **5-5** |  |  | Cr 70.8 N (51.9) I | | | | | [69] |
| **5-6** |  |  | Cr 56 N (49) I | | 22.0 | | | [46, 70] |
| **5-7** |  |  | Cr 48 I | | | | | [71] |
| **5-8** |  |  | Cr 74 N (19) I | | | | | [72] |
| **5-9** |  |  | Cr 98 I | | | | | [73] |
| **5-10** |  |  | Cr 40 I | | | | | [74] |
| **5-11** |  |  | Cr< 20 I | | | | | [57] |
| **5-12** |  |  | Cr 62 Sm (43) Sm (52) N 85 I | | 27.2 | | | [75, 76] |
| **5-13** |  |  | N – 25 I | | | | | [77] |
| **5-14** |  |  | Cr 56.6 N 64.8 I | | | | | [78] |
| **5-15** |  |  | Cr 45.6 N 46.7 I | | | | | [79] |
| **5-16** |  |  | Cr 104 N 129 I | | | | | [77] |
| **5-17** |  |  | Cr 113 N (50) I | | | | | [77] |

[a] Measuring temperature, $T_{meas} = T_{N\text{-}I} - 10°C$.

expressed by the following orders of increasing clearing points and nematic ranges:

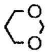


These results show that the introduction of the *trans*-1,4-cyclohexylene fragment into the molecular core of liquid crystals of system (XIII) results in the broadest nematic range with highest thermostability, while for the system (XIV) it gives the narrowest nematic range with moderate thermostability.

It is interesting to note that the replacement of two of the four 1,4-phenylene fragments incorporated in the molecular core of compound **4-7** by two *trans*-1,4-cyclohexylene fragments, leads to decreasing melting and clearing points and the creation of the nematic phase in the case of symmetrical molecular structure with two *trans*-1,4-cyclohexylene fragments with attached alkyl chains (compounds **4-7** and **4-8**); for compound **4-9**, however, it results in low melting and highly smectic character of its mesophase.

As can be seen from table 4, the replacement of two *trans*-1,4-cyclohexylene fragments by two *trans*-1,4-silacyclohexylene and two 1,3-cyclopentylene fragments

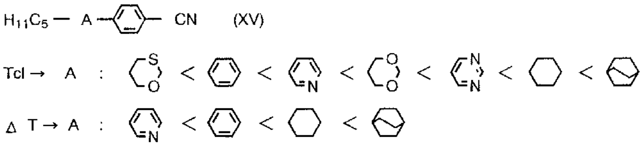
Table 6. Physico-chemical properties of some liquid crystals: $H_{11}C_5$–A–B–X.

| Compound | A | B | X | Phase transitions/°C | $d_1$/Å | $d_2$/Å | $\zeta_1$/Å | $\zeta_2$/Å | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| **6-1** |  |  | CN | Cr 45.4 N 55.4 I | | 24.8$^a$ | | 60$^a$ | [65, 80] |
| **6-2** |  |  | CN | Cr 73 I | | | | | [81] |
| **6-3** |  |  | CN | Cr 48 N 64.2 I | | 27.3$^a$ | | 74$^a$ | [37, 65] |
| **6-4** |  |  | CN | Cr 47.4 N 68 I | 15.4$^a$ | 26.0$^a$ | 45$^a$ | 66$^a$ | [7, 65, 82] |
| **6-5** |  |  | CN | Cr 84 N (36) I | | | | | [83] |
| **6-6** |  |  | CN | Cr 108.5 I | | | | | [69] |
| **6-7** |  |  | CN | Cr 70 Sm 94 N 98 I | | | | | [23] |
| **6-8** |  |  | CN | Cr 96 N 109 I | | | | | [69] |
| **6-9** |  |  | CH=CH–CN | Cr 49 SmA 61 N 149.5 I | | 30.0$^b$ | | 280$^b$ | [84, 85] |
| **6-10** |  |  | CH=CH–CN | Cr 67.5 N 155.1 I | 17.9$^b$ | 25.6$^b$ | 90$^b$ | 150$^b$ | [80, 85] |
| **6-11** |  |  | CH=CH–CN | Cr 80 SmA 99 N 147.1 I | | | | | [86] |
| **6-12** |  |  | NCS | Cr 67.5 N (49.5)I | | | | | [87] |
| **6-13** |  |  | NCS | Cr 53 SmE 74.5 I | | | | | [87] |
| **6-14** |  |  | NCS | Cr 34 SmA 98.5 I | | | | | [88] |
| **6-15** |  |  | NCS | Cr 46 Sm 85.5 I | | | | | [89] |
| **6-16** |  |  | NCS | Cr 60 SmA 79 I | | | | | [90] |
| **6-17** |  |  | NCS | $Cr_2$ 64.5 $Cr_1$ 74 N 99.5 I | | | | | [91] |

$^a$ Measuring temperature, $T_{meas} = T_{N\text{-}I} - 10$°C.
$^b$ $T_{meas} = T_{N\text{-}I} - 75$°C.

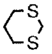
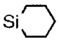
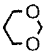
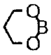
in the compounds **4-1** and **4-8** to give compounds **4-6** and **4-10**, respectively, leads to decreasing smectic and nematic thermostabilities. It should be noted that increasing the quantity of the *trans*-1,4-cyclohexylene fragments replaced by the *trans*-1,4-silacyclohexylene fragments in compound **4-1** results in decreasing smectic and nematic thermostabilities and nematic ranges (compounds **4-5** and **4-6**).

The effect on mesomorphic behaviour of introducing the *trans*-1,4-cyclohexylene fragment into the molecular core of two-ring strong polar cyano derivatives is shown in tables 5 and 6; for compounds **5-1**–**5-11** having the 4′-cyanophenyl fragment it can be described as follows:



These results show that the introduction of the *trans*-1,4-cyclohexylene fragment into the molecular core of system (XV) gives liquid crystals exhibiting a

Table 7. Physico-chemical properties of some liquid crystals: $H_{11}C_5$–A–B––CN.

| Compound | A | B | Phase transitions/°C | Δε | Δ*n* | ν/mm² s⁻¹ | $d_1$/Å | $d_2$/Å | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| **7-1** |  |  | Cr 96 N 222 I | 9.1[a] | 0.114[b] | 78[d] | 20.7 | 30.7 | [65, 92–94] |
| **7-2** |  |  | Cr 130 N 239 I | 13.5[c] | 0.356[d] | 90[d] | 20.4 | 30.9 | [66, 80, 95, 96] |
| **7-3** |  |  | Cr 90 Sm 162 N 254 I | 21.4[d] | 0.344[d] | | | | [80] |
| **7-4** |  |  | Cr 124 Sm 204.5 N 259.5 I | | | | | | [97] |
| **7-5** |  |  | Cr 159 N 269 I | | | | 18.0 | 30.7 | [68, 95] |
| **7-6** |  |  | Cr 134 N 178 I | | | | | | [98] |
| **7-7** |  |  | Cr 114.7 SmB 160.7 N 210.6 I | | | | | | [99] |
| **7-8** |  |  | Cr 79.1 Sm (78.5) N 114.3 I | | | | | | [100] |
| **7-9** |  |  | Cr 50.5 N 61 I | 10.1[b] | 0.075[b] | 62[e] | | | [57, 93] |
| **7-10** |  |  | Cr 63 S 75.4 N 106.7 I | 6.5[a] | 0.110[b] | | | | [93] |
| **7-11** |  |  | Cr 53.8 Sm 60.3 N 234.4 I | 13.0[d] | 0.170[d] | 94[d] | | | [101, 102] |
| **7-12** |  |  | Cr 87 N 222.1 I | 13.3[d] | 0.214[d] | 130[d] | | | [94, 103] |
| **7-13** |  |  | Cr 100.5 N 231 I | 23.0[d] | 0.240[d] | 200[d] | | | [94, 104] |
| **7-14** |  |  | Cr 113 N 228 I | 14.0[c] | 0.232[d] | 6.2[f] | | | [80] |
| **7-15** |  |  | Cr 92 N 170 I | | | | | | [105] |

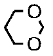
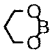
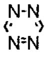
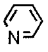
[a] $\tau = T_{meas}/T_{N\text{-}I} = 0.95$; $T_{meas}$, $T_{N\text{-}I}$/K.
[b] Extrapolated from 10 wt % solution in ZLI-1132 at $\tau = 0.95$.
[c] $\tau = 0.75$.
[d] Extrapolated from 10 wt % solution in ZLI-1132 at 20°C.
[e] Extrapolated from 10 wt % solution in the mixture of cyanobiphenyls at 20°C.
[f] $[\gamma_1]/P$, extrapolated from 10 wt % solution in ZLI-1132 at 25°C.

broad nematic range with high thermostability, which, however, is lower than that of the corresponding 1,4-bicyclo[2.2.2]octylene derivative **5-4**.

From the comparison of the results obtained for the systems (I), (IV) and (XV), it follows that the influence on mesomorphic properties of introducing the trans-1,4-cyclohexylene fragment strongly depends on molecular structures, particularly on terminal substituents. The effect of the molecular core structure is also revealed by considering the phase transition temperatures of the following compounds presented in table 6. Replacement of the *trans*-1,4-cyclohexylene fragment in compounds **6-1** and **6-5** by the 1,4-phenylene fragment to give compounds **6-2** and **6-6**, respectively, leads to increasing melting points and decreasing nematic thermostability or disappearance of the nematic phase; the same replacement in compounds **6-3** and **6-7** to create compounds **6-4** and **6-8**, respectively, results in slightly decreasing (compound **6-4**) and significantly increasing (compound **6-8**) the melting points and increasing the nematic thermostabilities.

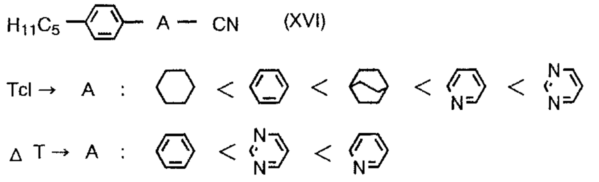
The position of the *trans*-1,4-cyclohexylene fragment introduced into the molecular core of two-ring cyano derivatives plays a very important role in their mesomorphic behaviour. This can be seen by comparing the phase transition temperatures of compounds **5-1** and **5-13**, showing that the latter exhibits a lower value of the nematic–isotropic liquid phase transition temperature. The replacement of the *trans*-1,4-cyclohexylene fragment in compound **5-13** by other molecular fragments creates

Table 8. Physico-chemical properties of some liquid crystals: $H_{2n+1}C_n$–A–B–K–CN.

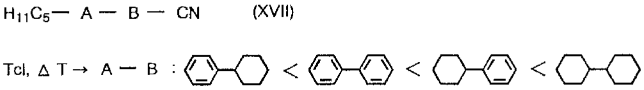
| Compound | $n$ | A | B | K | Phase transitions/°C | $\gamma_1$/P | $\Delta\varepsilon$ | $\Delta n$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| **8-1** | 5 |  |  |  | Cr 80 N 160 I | | | | [106] |
| **8-2** | 5 |  |  |  | Cr 76 N 232.1 I | 11.8[a] | 16.7[b] | 0.344[c] | [80] |
| **8-3** | 5 |  |  |  | Cr 125.5 N 243 I | | | | [97] |
| **8-4** | 5 |  |  |  | Cr 110 N 165 I | | | | [46] |
| **8-5** | 5 |  |  |  | Cr 103 N 132.7 I | | | | [107] |
| **8-6** | 5 |  |  |  | Cr 161 X 210 I[d] | | | | [108] |
| **8-7** | 5 |  |  |  | Cr 131 SmA 140 N 263 I | | | | [109] |
| **8-8** | 5 |  |  |  | Cr 109.5 N 175 I | | | | [104] |
| **8-9** | 5 |  |  |  | Cr 112 N 175.5 I | | | | [104] |
| **8-10** | 3 |  |  |  | Cr 133 N 230 I | | | | [106] |
| **8-11** | 3 |  |  |  | Cr 73.1 Sm 81.1 N 238.9 I | | | | [101] |
| **8-12** | 3 |  |  |  | Cr 95 Sm 197 N 236 I | | | | [110] |
| **8-13** | 3 |  |  |  | Cr 123 N 160 I | | | | [106] |
| **8-14** | 3 |  |  |  | Cr 182 N 257.5 I | | | | [66] |
| **8-15** | 3 |  |  |  | Cr 112.6 N 254.6 I | | | | [111] |
| **8-16** | 3 |  |  |  | Cr 88.5 Sm 102.7 N 245.2 I | | | | [111] |

[a] Extrapolated from 10 wt % solution in ZLI-1132 at 25°C.
[b] $\tau = 0.7$.
[c] Extrapolated from 10 wt % solution in ZLI-1132 at 20°C.
[d] X is unknown mesophase.

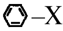
liquid crystals with enhanced nematic thermostabilities (compounds **5-13**, **5-2**, **5-17**, **6-2**, **6-4**, **6-6**, **6-8**; tables 5, 6):

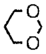
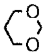
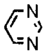
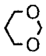

(XVI)

The results obtained for the systems (XV and XVI) show that the influence of the *trans*-1,4-cyclohexylene fragment depends on its position. From table 5, it follows that replacing the 1,4-phenylene fragment by the *trans*-1,4-cyclohexylene fragment in compound **5-1** to give the compound **5-12** results in increased melting and clearing points and the creation of monotropic smectic phases. The effect of introducing *trans*-1,4-cyclohexylene fragments, their quantity and positions in the molecular core of two-ring cyano derivatives, can be described as follows (compounds **5-1**, **5-2**, **5-12**, **5-13**, table 5):


(XVII)

These results show that the introduction of the second *trans*-1,4-cyclohexylene fragment in the molecular core of two-ring cyano derivatives of system (XVII) gives liquid crystals with the broadest nematic range having the highest thermostability; compound **5-13**, having only one *trans*-1,4-cyclohexylene fragment with attached

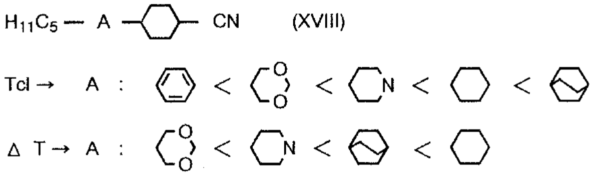
Table 9. Physico-chemical properties of some liquid crystals: $H_{2n+1}C_n$–A––X.

| Compound | $n$ | A | X | Phase transitions/°C | $\Delta\varepsilon$[a] | $\Delta n$[a] | $\nu$[a]/$mm^2\ s^{-1}$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| **9-1** | 5 |  | $OCHF_2$ | Cr 1 N (– 17) I | 7.6 | 0.058 | 7.0 | [112] |
| **9-2** | 5 |  | $OCHF_2$ | Cr 23 Sm (4) N (8) I | 14.6 | 0.044 | 9.0 | [88] |
| **9-3** | 5 |  | $OCHF_2$ | Cr 20.1 Sm 24 I | 20.6 | 0.123 | 14.0 | [88, 112] |
| **9-4** | 5 |  | $OCHF_2$ | Cr 26 Sm 43.6 I | 15.9 | 0.125 | 12.0 | [88] |
| **9-5** | 7 |  | $OCHF_2$ | Cr 7 I | 5.6 | 0.055 | 8.0 | [88] |
| **9-6** | 7 |  | $OCHF_2$ | Cr 24.6 Sm (22.7) N 24.3 I | 9.6 | 0.044 | 12.4 | [88] |
| **9-7** | 7 |  | $OCHF_2$ | Cr 10.8 N 31.6 I | 3.8[b] | 0.063[b] | 14.0[b] | [88] |
| **9-8** | 7 |  | $OCHF_2$ | Cr 22.1 Sm 46.1 I | | | | [88] |
| **9-9** | 7 |  | $OCHF_2$ | Cr 26 SmA 32 I | 19.8 | 0.112 | 16.0 | [112] |
| **9-10** | 5 |  | $OCF_3$ | Cr 14 I | 7.1 | 0.046 | | [112] |
| **9-11** | 5 |  | $OCF_3$ | Cr 23.6 SmB 34.9 I | 10.0 | 0.040 | | [88] |
| **9-12** | 5 |  | $OCF_3$ | Cr 32 SmA 42.5 I | 18.5 | 0.094 | | [88] |
| **9-13** | 5 |  | $OCF_3$ | Cr 18.6 SmB 38.5 SmA 52.4 I | 11.8 | 0.074 | | [88] |
| **9-14** | 5 |  | $OCF_3$ | Cr 67 I | | | | [113] |

[a] Extrapolated from 10 wt % solution in ZLI-1132 at 20°C.
[b] $T_{meas} = 20°C$.

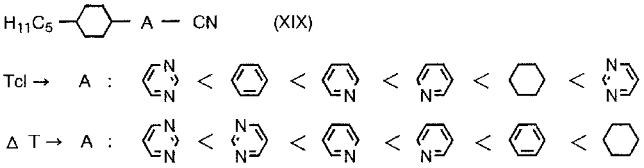
terminal cyano group, exhibits the lowest nematic thermostability.

The effect of replacing the *trans*-4-pentylcyclohexyl fragment in the compound **5-12** by other pentyl substituted fragments to create compounds **5-13–5-16** can be expressed as follows:



Here, the *trans*-4-pentyl-(*trans*-4′-cyanocyclohexyl)-cyclohexane exhibits the broadest nematic range with high thermostability compared with those of other derivatives of system (XVIII).

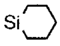
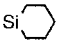
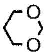
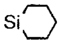
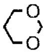
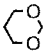
The effect of replacing the *trans*-4′-cyanocyclohexyl fragment in compound **5-12** by other cyano substituted fragments to give compounds **5-1**, **6-1**, **6-3**, **6-5**, **6-7** is clearly shown in tables 5 and 6 and can be expressed by the following orders of increasing $T_{cl}$ and $\Delta T$:



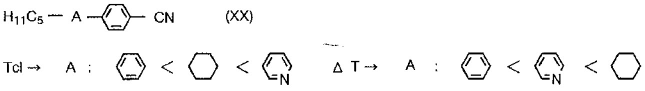
The results obtained for systems (XVI) and (XIX) reveal that the efficiency of the *trans*-1,4-cyclohexylene fragments introduced into their molecular cores depends on their structures.

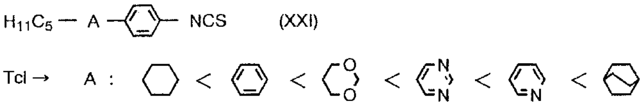
The replacement of the terminal CN group in system (XV) by the CH=CH–CN and the NCS groups to create systems (XX) and (XXI), respectively, results in changing the orders of increase of the clearing points and nematic ranges (compounds **6-9–6-11**; **6-12–6-17**, table 6):

Table 10. Physico-chemical properties of some liquid crystals: $H_7C_3$–A–B–K–X.

| Compound | A | B | K | X | Phase transitions/°C | $\Delta\varepsilon^a$ | $\Delta n^a$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| **10-1** |  |  |  | $OCHF_2$ | Cr 82 Sm 121 N 169.4 I | 10.2 | 0.170 | [88] |
| **10-2** |  |  |  | $OCHF_2$ | Cr 50.8 Sm 69.2 N 172.2 I | 8.3 | 0.114 | [88] |
| **10-3** |  |  |  | $OCF_2Cl$ | Cr 96 Sm 112.5 N 123 I | 9.2 | 0.154 | [115] |
| **10-4** |  |  |  | $OCF_2Cl$ | Cr 82 N 133 I | 7.5 | 0.100 | [115] |
| **10-5** |  |  |  | F | Cr 98.3 N 153.4 I | $4.7^b$ | $0.096^b$ | [116] |
| **10-6** |  |  |  | F | Cr 54.1 Sm 96.6 N 155.2 I | $4.6^b$ | $0.089^b$ | [116] |
| **10-7** |  |  |  | F | Cr 80.2 N 119.3 I | | | [100] |
| **10-8** |  |  |  | F | Cr 65 N 109 I | | | [117] |
| **10-9** |  |  |  | F | Cr 82.4 N 146.2 I | | | [103] |
| **10-10** |  |  |  | F | Cr 99 Sm (76.5) N 157.3 I | | | [118] |
| **10-11** |  |  |  | $OCF_3$ | Cr 90 SmB 129 N 151.4 I | | 0.166 | [112] |
| **10-12** |  |  |  | $OCF_3$ | Cr 38 SmB 69 N 153.7 I | | 0.088 | [112] |
| **10-13** |  |  |  | $OCF_3$ | Cr 90 Sm 104 SmA 129 I | | | [119] |
| **10-14** |  |  |  | $OCF_3$ | Cr 44 Sm 112 SmB 147 N 189 I | | | [119] |
| **10-15** |  |  |  | $OCF_3$ | Cr 42 N 106 I | | | [117] |
| **10-16** |  |  |  | $OCF_3$ | Cr 125.2 SmB 195.8 I | | | [25] |

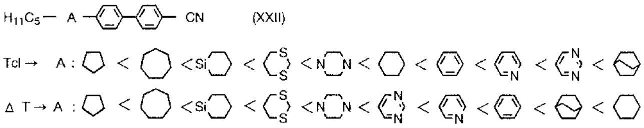
[a] Extrapolated from 10 wt % solution in ZLI-1132 at 20°C.
[b] Extrapolated from 20 wt % solution in the mixture of difluoro substituted derivatives at 25°C.





The results obtained for the systems (XV), (XX), (XXI) show that the effect of the *trans*-1,4-cyclohexylene fragments introduced into their molecular cores depends on the structure of their terminal substituents.

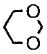
The effect of introducing the *trans*-1,4-cyclohexylene fragment into the molecular core of three-ring cyano derivatives is illustrated by the data collated in tables 7 and 8; for the liquid crystals having the cyanobiphenyl fragment it can be expressed by the following orders of increase of clearing points and nematic ranges (compounds **7-1**–**7-10**, table 7):



These data reveal that the introduction of the *trans*-1,4-cyclohexylene fragment into the molecular core of system (XXII) creates liquid crystals having the broadest nematic range with moderate nematic thermostability compared with those of other derivatives of this system.

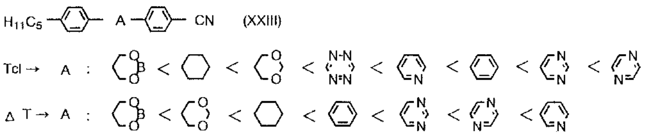
The introduction of the *trans*-1,4-cyclohexylene fragment as the middle ring in the molecular core of three-ring cyano derivatives of system (XXIII) produces liquid crystals having a moderate nematic range with low nematic thermostability compared with those of

Table 11. Physico-chemical properties of some liquid crystals: $H_{11}C_5$–A–B–CN.

| Compound | A | B | $\mu$/D | $\varepsilon_\perp$ | $\Delta\varepsilon$ | $g^d$ | $\Delta n$ | $k_p$ (40°C) | $\nu$/mm$^2$ s$^{-1}$ | $K_{33}/K_{11}$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **5-1** |  |  | 4.63 | 5.3$^a$ | 11.2$^a$ | 0.590 | 0.109$^a$ | 0.6333 | 21.5$^f$ | 1.77$^e$ | [5, 8, 70, 164–167] |
| **5-2** |  |  | 4.80 | 6.6$^e$ | 13.3$^e$ | 0.530$^c$ | 0.178$^e$ | 0.6523 | 26.3$^f$ | 1.43$^e$ | [5, 70, 166–168] |
| **5-3** |  |  | 6.00 | 10.9$^a$ | 17.8$^a$ | 0.518 | 0.214$^b$ | 0.6538 | 50$^b$ |  | [5, 80, 166] |
| **5-4** |  |  | 3.91 |  | 10.0$^f$ | 0.732$^k$ | 0.140$^f$ | 0.6590$^j$ |  | 2.35$^e$ | [15, 166, 169] |
| **5-5** |  |  | 6.00 | 8.0$^b$ | 34.0$^b$ | 0.580 | 0.224$^b$ |  | 55$^b$ | 1.13$^e$ | [70, 94, 168] |
| **5-6** |  |  | 6.00 | 8.0$^b$ | 17.4$^b$ | 0.585$^c$ | 0.055$^l$ |  | 47$^b$ | 1.36$^e$ | [70, 94, 168, 176] |
| **5-12** |  |  | 3.77 | 9.2$^a$ | 4.5$^a$ | 0.690$^i$ | 0.051$^a$ | 0.6300$^j$ | 60$^b$ | 1.59$^e$ | [15, 94, 169, 170] |
| **6-1** |  |  | 5.84 | 10.8$^a$ | 12.1$^a$ | 0.615 | 0.084$^g$ | 0.6353 | 41$^b$ |  | [5, 80] |
| **6-3** |  |  | 4.03 | 6.5$^a$ | 3.7$^a$ | 0.676 | 0.127$^b$ | 0.6381 |  |  | [5, 80, 120] |
| **6-2** |  |  | 6.00 |  | 17.9$^b$ | 0.466 | 0.204$^b$ | 0.6656 |  |  | [5, 80] |
| **6-4** |  |  | 4.48 | 8.0$^a$ | 6.5$^a$ | 0.537 | 0.205$^h$ | 0.6631 |  |  | [5, 80, 169] |

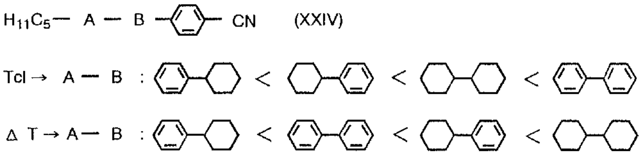
[a] $\tau = T_{meas}/T_{N\text{-}I} = 0.95$; $T_{meas}$, $T_{N\text{-}I}$/K.
[b] Extrapolated from 10 wt% solution in ZLI-1132 at 20°C.
[c] Extrapolated to $T_{meas} = T_{N\text{-}I}$ [168].
[d] $T_{meas} = T_{N\text{-}I}$.
[e] $\tau = 0.96$.
[f] $T_{meas} = 22°C$.
[g] $\tau = 0.99$.
[h] $\tau = 0.94$.
[i] Calculated using the data taken from [169, 170].
[j] $T_{meas} = 61°C$.
[k] Calculated using the data taken from [146, 169].
[l] $T_{meas} = T_{N\text{-}I} - 10$ K.

other derivatives of this system (compounds **8-1**–**8-7**, table 8):



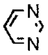
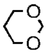
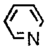
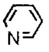
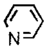
The results obtained for systems (XXII) and (XXIII) show that the effect of introducing the *trans*-1,4-cyclohexylene fragment depends on its position in their cores. As can be seen from tables 7 and 8, the introduction of the second *trans*-1,4-cyclohexylene fragment into the molecular core of three-ring cyanophenyl derivatives results in increasing nematic thermostability and range, decreasing melting point and creation of the smectic phase (compounds **7-1** and **7-11**; **8-10** and **8-11**). In the case of three-ring cyanopyridine derivatives, such an introduction decreases the clearing and melting points while maintaining approximately the same nematic range, and creates the smectic phase (compounds **8-15** and **8-16**).

The effect of introducing *trans*-1,4-cyclohexylene fragments, their quantity and positions in the molecular core of three-ring cyano derivatives on mesomorphic properties is as follows (compounds **7-1**, **7-2**, **7-11**, **8-1**, tables 7, 8):



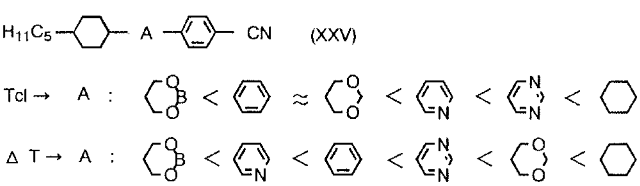
These results show that the introduction of the *trans*-1,4-cyclohexylene fragment as the middle ring in the molecular core of system (XXIV) produces liquid crystals with the lowest nematic thermostability and range,

Table 12. Physico-chemical and electro-optical ($d$-cell gap = 10 µm, $U$ = 3 V) properties of binary mixtures ($C_5$ and $C_7$ = 40:60 mol %) of the liquid crystals [7, 169]: R–A–B–CN.

| Compound | A | B | $T_{N\text{-}I}$ /°C | $d_2{}^a$ /Å | $\gamma_1{}^b$ /P | $E^b$ /eV | $K_{33}/K_{11}{}^c$ | $\varepsilon_\perp{}^c$ | $\Delta\varepsilon^c$ | $\Delta n^c$ | $U_{90}{}^b$ /V | $U_{10}{}^b$ /V | $\tau^1_{on}{}^b$ /ms | $\tau^2_{on}{}^b$ /ms | $\tau_{off}{}^b$ /ms | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **12-1** |  |  | 56.4 | 28.5 | 1.00 | 0.410 | 1.68 | 5.4 | 9.2 | 0.100 | 1.67 | 2.32 | 133 | 33 | 46 | |
| **12-2** |  |  | 39.0 | 27.4 | 1.10 | 0.546 | 1.37 | 6.0 | 11.7 | 0.184 | 1.30 | 1.78 | 85 | 21 | 69 | |
| **12-3** |  |  | 44.1 | 25.6 | 1.84 | 0.540 | 1.25 | 10.7 | 16.0 | 0.175 | 1.08 | 1.54 | 75 | 20 | 105 | |
| **12-4** |  |  | 51.0 | 23.0 | 1.90 | 0.565 | 1.06 | 8.7 | 19.6 | 0.174 | 1.07 | 1.48 | 70 | 20 | 90 | |
| **12-5** |  |  | 49.8 | | $1.34^a$ | | $1.43^a$ | $8.9^a$ | $13.3^a$ | $0.089^{a,d}$ | | | | | | [171, 172] |
| **12-6** |  |  | 96.5 | 27.8 | 3.6 | 0.426 | 1.93 | | 8.6 | 0.114 | | | | | | [65, 173] |
| **12-7** |  |  | 57.7 | 27.0 | 1.78 | 0.480 | 1.53 | 10.0 | 12.4 | 0.093 | 1.53 | 2.16 | 114 | 30 | 95 | |
| **12-8** |  |  | 49.0 | 26.6 | 2.20 | 0.495 | 1.31 | 11.3 | 15.3 | 0.175 | 1.25 | 1.82 | 130 | 30 | 105 | |
| **12-9** |  |  | 64.3 | | 1.40 | 0.485 | 1.37 | 7.5 | 3.3 | 0.104 | 2.50 | 3.45 | $130^e$ | $20^e$ | $43^e$ | |
| **12-10** |  |  | 69.1 | 27.9 | 3.50 | 0.505 | $1.11^f$ | 8.7 | 7.3 | 0.172 | 1.90 | 2.63 | 130 | 30 | 60 | |

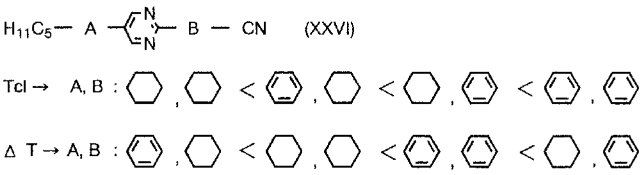
[a] $T_{meas} = T_{N\text{-}I} - 10$°C.
[b] $T_{meas} = 25$°C.
[c] $T_{meas}/T_{N\text{-}I}$ K = 0.95.
[d] $\lambda = 520$ nm.
[e] $U = 5$ V.
[f] $T_{meas}/T_{N\text{-}I}$ K = 0.98.

while 1-[*trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl]-4-cyanobenzene exhibits the broadest nematic range, with moderate thermostability, among the compounds belonging to this system. The thermal data presented in table 7 show that the replacement of the middle *trans*-1,4-cyclohexylene fragment in compound **7-11** by other molecular fragments to give compounds **7-12**–**7-15** decreases the nematic thermostabilities and ranges:



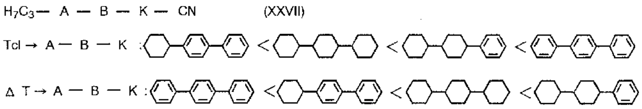
As in the case of two-ring cyano derivatives, the results obtained for systems (XXIII) and (XXV) reveal that the efficiency of the *trans*-1,4-cyclohexylene fragment introduced into their molecular cores depends on their structures.

The effect on mesomorphic properties of replacing one or two 1,4-phenylene fragments by one or two *trans*-1,4-cyclohexylene fragments in compound **8-3** to give compounds **7-13**, **8-8**, **8-9** can be expressed as follows:



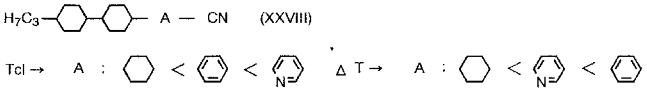
These results show that the introduction of two *trans*-1,4-cyclohexylene fragments into the molecular core of system (XXVI) gives liquid crystals exhibiting the lowest nematic thermostability and moderate nematic range in comparison with those of other derivatives of this system.

The effect of introducing three *trans*-1,4-cyclohexylene fragments into the molecular core of three-ring cyano derivatives is clearly shown in table 8 for compounds **8-10**–**8-12**, **8-14** and is expressed by the following orders of increasing $T_{cl}$ and $\Delta T$:

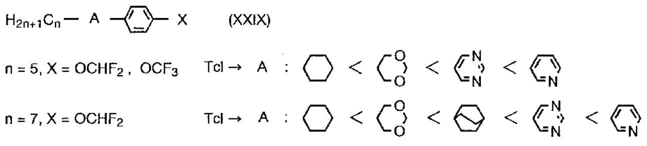


These data show that the introduction of three *trans*-1,4-cyclohexylene fragments into the molecular core of system (XXVII) creates liquid crystals with moderate nematic thermostability and range, lower than those of the corresponding bicyclohexylphenyl derivative.

As can be seen from table 8, replacing the *trans*-4′-cyanocyclohexyl fragment by other fragments in compound **8-12**, to give the compounds **8-11** and **8-16**, leads to increasing nematic ranges and thermostabilities:



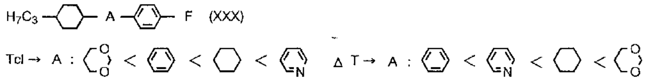
The thermal data collated in table 9 show that two-ring trans-1,4-disubstituted cyclohexylene derivatives having $OCHF_2$, or $OCF_3$ terminal groups exhibit a monotropic nematic phase, or are not mesomorphic, compared with other corresponding derivatives (compounds **9-1–9-4**; **9-5–9-9**; **9-10–9-13**; excepting **9-14**):



Interestingly, increase in the alkyl chain length or replacement of a $OCHF_2$ terminal group by the $OCF_3$ group do not affect the order of increasing $T_{c1}$ obtained for system (XXIX); introduction of a terminal CN group in system (XXIX, $n = 5$) to create system (XV) changes the order of increasing clearing temperatures.

In contrast to the mesomorphic behaviour of two-ring cyano derivatives presented in table 5 (compounds **5-1** and **5-12**), replacement of the 1,4-phenylene fragment by *trans*-1,4-cyclohexylene in compound **9-1** results in the disappearance of the monotropic nematic phase [114].

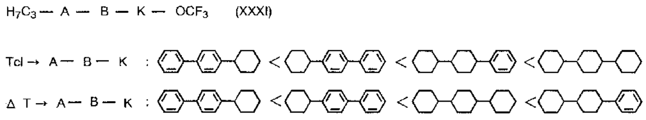
The effects of introducing the *trans*-1,4-cyclohexylene fragments into the molecular core of three-ring liquid crystalline derivatives having halogenated terminal substituents are shown in table 10. It should be noted that introduction of the second *trans*-1,4-cylohexylene fragment increases the nematic ranges and thermostabilities (compounds **10-1** and **10-2**; **10-3** and **10-4**; **10-5** and **10-6**; **10-11** and **10-12**). As was observed for the weakly polar *trans*-1,4-disubstituted derivatives presented in table 4, replacing the *trans*-1,4-cyclohexylene fragment by the *trans*-1,4-silacyclohexylene fragment in compounds **10-5**, **10-6** and **10-12** to give compounds **10-7**, **10-8** and **10-15**, respectively, results in a decrease of nematic thermostabilities. The effect of replacing the middle *trans*-1,4-cyclohexylene fragment by other fragments in compound **10-6** to give compounds **10-5**, **10-9**, **10-10** can be expressed as follows:



These results show that the introduction of the *trans*-1,4-cyclohexylene fragment into the molecular core of system (XXX) gives liquid crystals with moderate nematic range and thermostability compared with those of other derivatives of this system.

As can be seen from table 10, the replacement of two *trans*-1,4-cyclohexylene fragments by two *trans*-1,3-dioxane fragments in compound **10-12**, to create compound **10-16**, significantly increases the melting and clearing temperatures and causes the disappearance of the nematic phase.

The effects of introducing *trans*-1,4-cyclohexylene fragments into the molecular core of compounds **10-11–10-14** are as follows:



These results reveal that the introduction of three *trans*-1,4-cyclohexylene fragments into the molecular core of system (XXXI) produces liquid crystals having a moderate nematic range with highest thermostability compared with those of other derivatives of this system. The similar effects of introducing the *trans*-1,4-cyclohexylene fragment into four-ring liquid crystalline derivatives having halogenated terminal substituents can be observed for compounds **4-11–4-14**, as presented in table 4.

Similar effects on mesomorphic properties have been found for other liquid crystalline derivatives on introduction of the *trans*-1,4-cyclohexylene fragment [6–8, 10–12, 57, 80, 88, 93, 120–146]. According to the theory of Maier and Saupe the nematic–isotropic phase transition temperature is proportional to the anisotropy of polarizability of the molecules forming the nematic phase [147]. The *trans*-1,4-disubstituted cyclohexylene derivatives, having decreased values of the anisotropy of polarizability compared with those of the corresponding aromatic liquid crystalline derivatives [15, 148], should consequently exhibit decreased values of the nematic–isotropic liquid transition temperature in comparison with those of aromatic liquid crystals. However, some of the presented results and those reported in [15, 148] are found not to follow the Maier and Saupe theory. It has been suggested that molecular packing predominantly influences nematic thermostability [19, 149]. The anisotropic dispersion interactions, and consequently the anisotropy of polarizability, also influence the packing and hence the stability of the mesophases, but play a secondary role compared with steric factors [149].

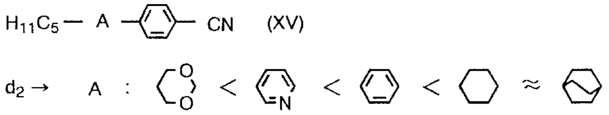
Other molecular aspects, such as association [150] or dipole–dipole attraction in polar liquid crystals, which can influence molecular packing also affect the stability of the mesophases [149].

### 2.2. *X-ray data*

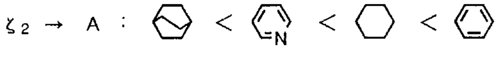
It has been shown that X-ray diffraction (XRD) of the nematic phase of liquid crystals is a useful method for studying the effects of the association of liquid crystal molecules on the structure of their nematic phases, and consequently on the liquid crystal properties [65, 70, 95, 151, 152].

XRD of polar liquid crystals has revealed the existence not only of a layer structure in the smectic phase, but also periodic density fluctuations in the nematic phase having a period *d*. Swarms containing tens to hundreds of molecules are involved and are characterized by a correlation length $\zeta$ defined directly from the width of the diffraction peak. For the nematic phase of some two-ring cyano derivatives it has been shown that the ratio $d/L$, where $L$ is the molecular length, is about 1.2–1.5 [65, 70, 151, 152]. Hence the period of the fluctuating layer structure significantly exceeds a single molecular length, and should be related to the size of the molecular dimer. Such a dimer is formed by two polar molecules being mutually antiparallel. Experimental values of the layer structure period *d*, for cyano derivatives belonging to various chemical classes, showed that *d* depends on the molecular structure of the polar liquid crystals, and characterizes the degree of overlap of the molecular cores on dimer formation. Further XRD investigations of the nematic phase of polar liquid crystals has revealed, in some cases, the simultaneous existence of two fluctuation layer structures with incommensurate periods $d_1$ and $d_2$, where $d_1 < L$ and $L < d_2 < 2L$ [65, 95, 151, 152].

It has been shown that for two-ring *trans*-1,4-disubstituted cyclohexylene derivatives having cyano and cyanoethynyl terminal groups, only one density wave with a characteristic period $d_2$ is observed [65, 76, 85, 151] (compounds **5-1**, **5-12**, **6-1**, **6-3**, **6-9**, tables 5 and 6), while the replacement of the *trans*-1,4-cyclohexylene fragment by the 1,4-phenylene fragment and pyridin-2,5-diyl fragment in compounds **5-1**, **6-3** and **6-9** to give compounds **5-2**, **5-3**; **6-4** and **6-10**, respectively, results in the appearance of two incommensurate density waves: monomeric with period $d_1$ (period $d_1$ is related to the fluctuation layer structure formed by separate molecules) and dimeric with decreased values of period $d_2$ [65, 85, 151]. As can be seen from tables 5 and 6, the $d_2$ values for two-ring cyano derivatives differ significantly, indicating different degrees of molecular core overlap in dimer formation [150, 153]. The different $d_2$ values probably result from significantly different electron density distributions in the molecular structure (for the pyridine derivatives this is shown in [154]) and steric factors which are responsible for the type of dimerization. This can be expressed by the following order of increasing $d_2$ depending on the type of molecular fragment A:



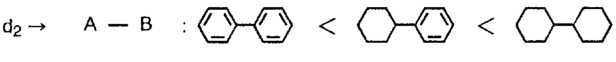
It has been shown that the correlation length $\zeta$ characterizes the potential smectogenicity of nematic liquid crystals [65, 151, 152]. For system (XV) the potential smectogenicity grows depending on the type of the molecular fragment A as follows:



These results show that the two-ring *trans*-1,4-disubstituted cyclohexylene cyano derivative **5-1** exhibits moderate smectogenicity compared with that of other derivatives belonging to system (XV).

As can be seen from table 5, increasing the number of *trans*-1,4-cyclohexylene fragments introduced into the molecular core of two-ring cyano derivatives further increases the length of their dimers:

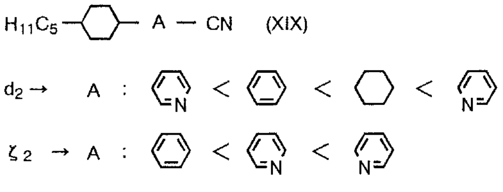
$H_{11}C_5—A—B—CN$ (XVII)



It is interesting that this order of increasing $d_2$ coincides with the order of increase of clearing points observed for the same system (XVII) as shown above.

A similar influence of the number of *trans*-1,4-cyclohexylene fragments incorporated in the molecular core on their $d_2$ values has been reported for other liquid crystalline derivatives [155].

The effect on the structure of their nematic phase of replacing the *trans*-4′-cyanocyclohexyl fragment in compound **5-12** by other cyano substituted molecular fragments is as follows:



The $d_2$ values for the three-ring cyanoderivatives **7-1**, **7-2** and **7-5** presented in table 7 are virtually the same. It seems that the major contribution to interactions in forming the dimer is made by the common cyano-biphenyl molecular fragment. The molecular cores are overlapped via this particular fragment, while the nature of the third ring (1,4-phenylene, *trans*-1,4-cyclohexylene, 1,4-bicyclo[2.2.2]octylene) does not play a particular role [65].

## 3. Static dielectric properties

The relationship between the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are, respectively, dielectric constants parallel and perpendicular to the nematic director **n** and the molecular structure of liquid crystals is described by the theory of Maier and Meier [156]:

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

where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$; $\Delta\alpha = (\alpha_\parallel - \alpha_\perp)$ is the polarizability anisotropy; $F$ is the cavity reaction field; $\mu$ is the dipole moment; $\beta$ is the angle between the molecular long axis and the dipole moment, $N$ is the number of molecules per unit volume and $S$ is the order parameter.

It has been shown that useful comparisons of the dielectric (as well as optical and elastic) properties of liquid crystals with different nematic–isotropic phase transition temperatures $T_{\text{N-I}}$ can only be made at constant reduced temperature $\tau = T_{\text{meas}}/T_{\text{N-I}}$ [157]. Tables 7–12 present data on the dielectric properties of liquid crystal compounds measured at a constant reduced temperature and extrapolated from liquid crystal mixtures at 20 or 25°C. According to [157], the extrapolations are not valid; however these estimations are the only way to obtain an estimate of the dielectric (as well as optical and elastic) properties of non-mesomorphic compounds, smectic liquid crystals, and liquid crystals with a narrow nematic range.

The data on the dielectric properties of the compounds and binary mixtures presented in tables 7–12 show that replacement of the *trans*-1,4-cyclohexylene fragment by 1,4-phenylene, pyridin-2,5-diyl, pyrimidin-2,5-diyl or *trans*-1,3-dioxan fragments increases the dielectric anisotropy due to the increase of molecular polarizability (compounds **5-1** and **5-2**, **5-3**, **5-5**, **5-6**; **6-1** and **6-2**; **6-3** and **6-4**; **7-1** and **7-2**, **7-3**; **7-11** and **7-12–7-14**; **7-14** and **8-2**; **9-1** and **9-2–9-4**; **9-5** and **9-6**, **9-9**; **9-10** and **9-11–9-13**; **10-1** and **10-2**; **10-3** and **10-4**; **10-5** and **10-6**; mixtures **12-1** and **12-2–12-5**; **12-7** and **12-8**; **12-9** and **12-10**). Replacement of the *trans*-1,4-cyclohexylene fragment by the 1,4-bicyclo[2.2.2]octylene fragment in compounds **5-1** and **9-5** to give compound **5-4** and **9-7**, respectively, decreases the dielectric anisotropy (tables 9 and 11). A similar decrease of dielectric anisotropy has been found for the 1,4-disubstituted cycloheptylene derivative **7-10**, while the corresponding 1,3-disubstituted cyclopentylene derivative **7-9** exhibits an increased value of $\Delta\varepsilon$ compared with that of the corresponding *trans*-1,4-disubstituted cyclohexylene derivative **7-1** (table 7). It should be noted that the replacement of the 4′-cyanophenyl fragment in compound **5-1** by the *trans*-4′-cyanocyclohexyl fragment giving compound **5-12** decreases the dielectric anisotropy. These results are found to be in an agreement with equation (1) [156].

Similar effects on their dielectric properties of introducing *trans*-1,4-cyclohexylene fragments into the molecular cores of other liquid crystal derivatives have been found [6–8, 10, 26, 57, 80, 88, 93, 120–122, 128, 130, 141, 158–161].

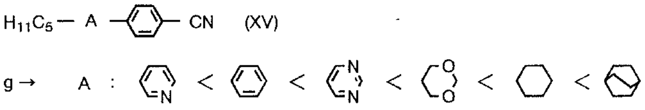
It has been shown that mesogenic molecules possessing strongly polar terminal groups form associated pairs. Both head-to-head and head-to-tail pairing occurs [153, 158, 162, 163], but antiparallel association predominates and reduces the effective dipole moment [150]:

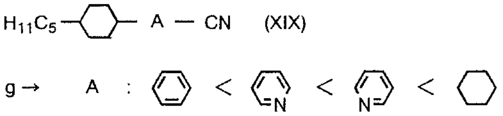
$$\mu^2_{\text{eff}} = g\mu^2 \qquad (2)$$

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

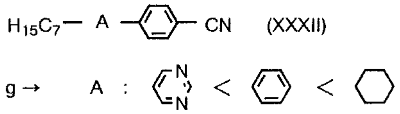
where $\varepsilon_i^\infty = 1.05n_i^2$; $g$ is the correlation factor characterizing the association tendency. For non-associating systems $g$ is equal to 1. The data collated in table 11 and in [7, 8, 150] show that all the compounds under investigation exhibit values of $g$ which are smaller than 1, indicating an antiparallel association. The replacement of the *trans*-1,4-cyclohexylene fragment by the 1,4-phenylene, pyridin-2,5-diyl, pyrimidin-2,5-diyl, trans-1,3-dioxan or 1,4-bicyclo[2.2.2]octylene fragments decreases $g$ (compounds **5-1** and **5-2**, **5-3**, **5-5**, **5-6**; **5-12** and **5-1**, **6-1**, **6-3**; **6-1** and **6-2**; **6-3** and **6-4**; table 11) or increases $g$ (compounds **5-1** and **5-4**, table 11).

The relationship between the correlation factor $g$ and the molecular structures of liquid crystalline two-ring cyano derivatives can be expressed by the following orders of increasing $g$ (table 11):


(XV)


(XIX)

Interestingly, an increase in the alkyl chain length in system (XV) from pentyl to heptyl to give system (XXXII), changes the order of increasing $g$ [150]:


(XXXII)

These results and those presented in [150, 162] show that the introduction of the *trans*-1,4-cyclohexylene fragment into the molecular core of two-ring cyano derivatives decreases the association tendency of their molecules compared with that for other molecular fragments. An increase in the number of *trans*-1,4-cyclohexylene fragments introduced further lowers this association tendency.

## 4. Optical properties

The phenomenological relation between refractive index and electric polarization is defined as [174, 175]:

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

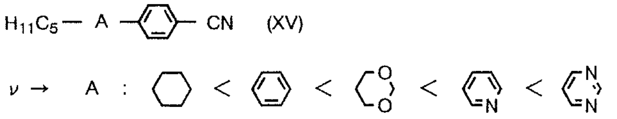
where the mean polarizability $\alpha^{*}=(\alpha_{\|}+2\alpha_{\perp})/3$; the mean refractive index $n^{*2}=(n_{\mathrm{e}}^{2}+2n_{\mathrm{o}}^{2})/3$; $n_{\mathrm{o}}$ is the ordinary and $n_{\mathrm{e}}$ is the extraordinary refractive index. From equation (4) and the previous section, it follows that aromatic compounds which have a large induced polarizability of their highly conjugated π-electron system exhibit an optical anisotropy $\Delta n=n_{\mathrm{e}}-n_{\mathrm{o}}$ which is much larger than that of the corresponding *trans*-1,4-disubstituted cyclohexylene derivatives; see compounds **5-1** and **5-2**, **5-3**, **5-5**; **5-12** and **6-1**, **6-3**; **6-1** and **6-2**; **6-3** and **6-4**; **7-1** and **7-2**, **7-3**; **7-11** and **7-12**–**7-14**; **7-14** and **8-2**; **9-1** and **9-3**, **9-4**; **9-5** and **9-9**; **9-10** and **9-12**, **9-13**; **10-1** and **10-2**; **10-3** and **10-4**; **10-5** and **10-6**; **10-11** and **10-12**; mixtures **12-1**–**12-4**; **12-7** and **12-8**; **12-9** and **12-10**; tables 7–12. Similar effects of increasing $\Delta n$ can be observed for the compounds **5-1** and **5-4**, **9-5** and **9-7**, while the 1,3-disubstituted cyclopentylene derivative **7-9** and the 1,4-disubstituted cycloheptylene derivative **7-10** show decreased values of $\Delta n$ compared with that of the corresponding *trans*-1,4-disubstituted cyclohexylene derivative **7-1** (tables 7, 9 and 11).

As can be seen from tables 9, 11 and 12, replacement of the *trans*-1,4-cyclohexylene fragment by the *trans*-1,3-dioxane fragment in the molecular cores of liquid crystals results in decreasing optical anisotropy (compounds **5-1** and **5-6**; **9-1** and **9-2**; **9-5** and **9-6**; **9-10** and **9-11**; mixtures **12-1** and **12-5**), see also [171]. An increase in the number of *trans*-1,4-cyclohexylene fragments introduced into the molecular core of two-ring cyano derivatives further lowers their optical anisotropy (compounds **5-1** and **5-12**; **10-1** and **10-2**; **10-3** and **10-4**; **10-5** and **10-6**; **10-11** and **10-12**, tables 10 and 11). These effects can be explained in terms of a reduction in the effective conjugation length of the π-electron system, resulting in a shorter resonance wavelength of the UV absorption spectrum for the liquid crystals incorporating the *trans*-1,4-cyclohexylene fragment than for corresponding aromatic liquid crystalline derivatives [177, 178].

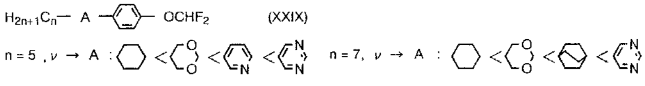
Similar effects of the *trans*-1,4-cyclohexylene fragment on the optical properties of other liquid crystalline derivatives have been reported [6–8, 10, 26, 57, 93, 120, 128, 130, 148, 165].

## 5. Visco-elastic properties

It has been shown that nematic liquid crystal materials for display applications should have a low viscosity for acceptable response times [157, 179]. According to the results on the kinematic viscosity ν and rotational viscosity $\gamma_1$ presented in tables 7, 9, 11 and 12, *trans*-1,4-disubstituted cyclohexylene derivatives exhibit lower values of the kinematic and rotational viscosity than those of the corresponding 1,4-phenylene, pyridin-2,5-diyl, pyrimidin-2,5-diyl, *trans*-1,3-dioxan, and 1,4-bicyclo[2.2.2]-octylene disubstituted derivatives (compounds **5-1**, **5-2**, **5-3**, **5-5**, **5-6**; **7-11** and **7-12**, **7-13**; **7-14** and **8-2**; **9-1** and **9-2**–**9-4**; **9-5** and **9-6**, **9-7**, **9-9**; mixtures **12-1**–**12-6**; **12-7** and **12-8**; **12-9** and **12-10**; tables 7–9, 11, 12):



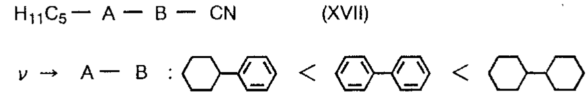
(XV)



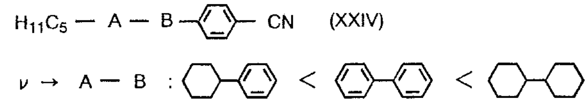
(XXIX)

It has been found that the replacement of the *trans*-1,4-cyclohexylene fragment by the 1,3-pentylene fragment in the molecular core of liquid crystals decreases the kinematic viscosity (compounds **7-1** and **7-9**, table 7; see also [57]).

An increase in the number of *trans*-1,4-cyclohexylene fragments in the molecular core of two-ring and three-ring cyano derivatives significantly increases the kinematic viscosity (compounds **5-1**, **5-2**, **5-12**; **7-1**, **7-2**, **7-11**; tables 7, 11):



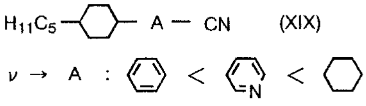
(XVII)



(XXIV)

The effect on viscous properties of increasing the number of *trans*-1,4-cyclohexylene fragments in the molecular cores of three-ring derivatives having halogenated terminal substituents is not clear: both increasing [112] and decreasing ν [112, 116] have been reported.

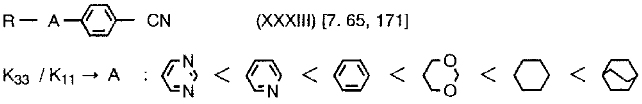
Replacement of the *trans*-4′-cyanocyclohexyl fragment in compound **5-12** by the 4′-cyanophenyl or 2-cyanopyridine fragments to give compounds **5-1** and **6-1**, respectively, lowers the kinematic viscosities (table 11):



(XIX)

The viscous behaviour of cyano derivatives can be explained in terms of the changed tendency for association [180] expressed by the correlation coefficient *g* (see §3). Similar effects on viscous properties of introducing the *trans*-1,4-cyclohexylene fragments into other liquid crystals have also been found [4–6, 128, 130, 167].

The elastic constant ratio $K_{33}/K_{11}$ of liquid crystal materials is a very important parameter in super twisted nematic-liquid crystal displays (STN-LCDs), defining their electro-optical performance [181]. As can be seen from tables 11 and 12, two-ring *trans*-1,4-disubstituted cyclohexylene cyano derivatives exhibit larger values of $K_{33}/K_{11}$ than those of other corresponding liquid crystals (compounds **5-1** and **5-2**, **5-5**, **5-6**; mixtures **12-1–12-5**; **12-7** and **12-8**; **12-9** and **12-10**), see also [15, 70, 130, 150, 159, 171]:


(XXXIII) [7. 65, 171]

The replacement of the *trans*-1,4-cyclohexylene fragment in compound **5-1** by 1,4-bicyclo[2.2.2]octylene to give compound **5-4** further increases the elastic constant ratio (table 11; see also mixtures **12-1** and **12-6**, table 12). Interestingly, an increase in the number of *trans*-1,4-cyclohexylene fragments in the molecular core of two-ring cyano derivatives lowers $K_{33}/K_{11}$ (compounds **5-1** and **5-12**, table 11). These results can be explained the XRD study of these compounds. It has been shown that elastic constant ratio $K_{33}/K_{11}$ is a linear function of the squared dimeric density wave period $d_2^2$ for binary mixtures of the two-ring cyano derivatives presented in table 12 [65]. In this interpretation dimers formed by the cyano derivatives play an important role. In combination with the increased development of the dimeric density wave, as compared with the monomeric one; this shows that for the fifth and greater homologues of two-ring *trans*-1,4-disubstituted cyclohexylene cyano derivatives, and for other cyano derivatives, the balance in the monomer-dimer system $2M \leftrightarrow D$ (considering data on the correlation factor $g$ in table 6 and on the correlation lengths $\zeta$ in [151]) is biased towards dimers defining the liquid crystal properties [7, 8, 65].

Similar effects on the elastic properties of other liquid crystals containing the *trans*-1,4-cyclohexylene fragment have been found [26, 159, 182].

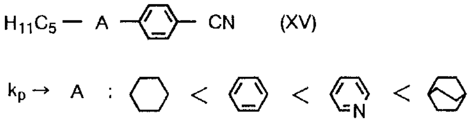
## 6. Molecular packing

It has been shown that liquid crystal molecular packing plays a very important role in the creation of their mesophases [19] and defines their optical properties [174]. The molecular packing coefficient is expressed in [166] as:

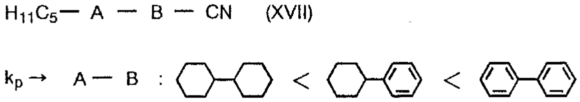
$$k_p = N_A V \rho / M \qquad (5)$$

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

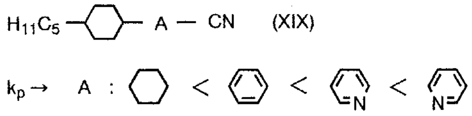
As can be seen from table 11, replacement of the *trans*-1,4-cyclohexylene fragment in compounds **5-1**, **5-12**, **6-1** and **6-3** by the 1,4-phenylene, pyridin-2,5-diyl or 1,4-bicyclo[2.2.2] octylene fragments to give compounds **5-2–5-4**; **5-1**, **6-1**, **6-3**; **6-2** and **6-4**, respectively, results in the increase of their molecular packing coefficients:


(XV)

An increase in the number of *trans*-1,4-cyclohexylene fragments in the molecular core of two-ring cyano derivatives further decreases the molecular packing coefficient (compounds **5-1**, **5-2**, **5-12**, table 11):


(XVII)

Replacement of the *trans*-4′-cyanocyclohexyl fragment in compound **5-12** by the 4′-cyanophenyl and 2-cyanopyridine and 5-cyanopyridine fragments to create compounds **5-1** and **6-1**, **6-3**, respectively, enhances the molecular packing:


(XIX)

These results can be associated with the difference in the energy of intermolecular interactions (and therefore with the difference in the activation energy of the rotational viscosity recorded for these compounds in table 12 [166]).

## 7. Comparative characteristics of liquid crystals

Selection of the best components for liquid crystal materials and the prediction of useful new chemical structures need comprehensive comparative investigations of the physico-chemical and electro-optical characteristics of liquid crystal compounds. It has been shown that the dielectric, diamagnetic, viscous, and elastic constants, as well as the nematic–isotropic transitions of solutions of homologues, approximately obey the additive rule [183]. This fact has been employed for comparison of the physico-chemical and electro-optical properties of liquid crystal *trans*-1,4-disubstituted cyclohexylene derivatives (and other corresponding derivatives) having narrow nematic ranges. This was done by using binary mixtures (containing a pentyl and a heptyl homologue) which give

Table 13. Physico-chemical and electro-optical parameters of the liquid crystalline mixtures. Measuring conditions of electro-optical parameters: $d = 10\,\mu\text{m}$, $T = 25°\text{C}$, $U_{\text{meas}} = 2U_{10}$ [67, 169].

| Mixture | $T_{\text{Sm-N}}$/°C | $T_{\text{N-I}}$/°C | $\varepsilon_{\perp}{}^{c}$ | $\Delta\varepsilon^{c}$ | $\Delta n^{*}$ | $U_{90}$/V | $U_{10}$/V | $\tau_{\text{off}}$/ms | $\tau^{1}_{\text{on}}$/ms | $\tau^{2}_{\text{on}}$/ms |
|---|---|---|---|---|---|---|---|---|---|---|
| **A1**$^{a}$ | $< -10$ | 68.8 | 6.1 | 3.0 | 0.111 | 2.55 | 3.55 | 35 | 150 | 30 |
| **A2**$^{a}$ | $< -10$ | 83.1 | 6.4 | 5.1 | 0.178 | 2.05 | 2.95 | 90 | 130 | 30 |
| **A3**$^{b}$ | $< -20$ | 65.8 | 7.7 | 12.0 | 0.160 | 1.45 | 1.95 | 60 | 90 | 25 |
| **A4**$^{b}$ | $< -20$ | 69.4 | 7.5 | 11.7 | 0.163 | 1.45 | 1.95 | 65 | 120 | 25 |
| **A5**$^{b}$ | $< -30$ | 67.7 | 7.6 | 13.2 | 0.164 | 1.45 | 2.00 | 60 | 100 | 25 |
| **A6**$^{b}$ | $< -10$ | 69.7 | 7.9 | 13.6 | 0.179 | 1.40 | 1.90 | 70 | 100 | 25 |

[a] The mixtures **A1**, **A2** were composed at 26 wt % of the 4-ethoxyphenyl ester of *trans*-4-butylcylohexanecarboxylic acid, 16 wt % of the 4-ethoxyphenyl ester of *trans*-4-hexylcyclohexanecarboxylic acid, 10 wt % of the 4-cyanobiphenyl ester of *trans*-4-butylcyclohexanecarboxylic acid, 19 wt % of the third and 29 wt % of the fifth homologues of 2-(*trans*-4-alkylcyclohexyl)-5-cyanopyridines and 2-(4-alkylphenyl)-5-cyanopyridines, respectively [169].

[b] The mixtures **A3**, **A4**, **A5**, **A6** were composed of 26 wt % of the 4-ethoxyphenyl ester of *trans*-4-butylcylohexanecarboxylic acid, 16 wt % of the 4-ethoxyphenyl ester of *trans*-4-hexylcyclohexanecarboxylic acid, 19 wt % of 5-propyl-2-(4-cyanophenyl)pyridine, 29 wt % of 5-pentyl-2-(4-cyanophenyl)pyridine and 10 wt % of the compounds **2-11**, **2-16**, **7-1**, **7-3**, respectively [169].

[c] $T_{\text{meas}} = 25°\text{C}$, $^{*}T_{\text{meas}} = 20°\text{C}$.

broad nematic ranges, with clearing points depending on the molecular structure as observed for pure compounds in §2. Table 12 shows that two-ring *trans*-1,4-disubstituted cyclohexylene cyano derivatives exhibit the lowest values of the response time $\tau_{\text{off}}$ and the largest values of the threshold voltage $U_{90}$ of the twist-effect, in comparison with those of other corresponding liquid crystals. These findings are consistent with the lowest values of the viscosity [179] observed for *trans*-1,4-disubstituted cyclohexylene derivatives (tables 11 and 12), and with the dependence of the threshold voltage of the twist-effect on the dielectric anisotropy and elastic constants [157]:

$$U_{90} \propto \pi[\kappa/\varepsilon_0 \Delta\varepsilon]^{1/2} \qquad (6)$$

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

In order to estimate the effect of using the *trans*-1,4-disubstituted cyclohexylene derivatives as components of liquid crystal mixtures, some mixtures containing these compounds and other well-known liquid crystals were prepared. Table 13 presents the physico-chemical and electro-optical properties of liquid crystal mixtures containing *trans*-1,4-disubstituted cyclohexylene derivatives and the corresponding 1,4-disubstituted phenylene, 2.5-disubstituted pyridine and 1,4-disubstituted bicyclo-[2.2.2]octylene derivatives. From this table, it follows that the use of trans-1,4-disubstituted cyclohexylene derivatives gives the lowest values of the response time $\tau_{\text{off}}$ of the twist-effect, compared with the effect of other liquid crystal derivatives (mixtures **A1** and **A2**, **A3** and **A4**, **A5** and **A6**). Replacement of the *trans*-1,4-disubstituted cyclohexylene derivatives by the other corresponding derivatives effects the clearing points, dielectric and optical properties of these mixtures in ways which are consistent with those observed for pure compounds in the previous sections.

## 8. Conclusions

The effects of *trans*-1,4-cyclohexylene fragments, in relation to their quantity and positions in the molecular core of liquid crystals, on liquid crystal physico-chemical and electro-optical properties have been studied; some general trends have been identified and explained. We believe that the results of these studies will broaden the understanding of fundamental structure–property relationships in liquid crystals, for the better satisfaction of the requirements for components of liquid crystal materials for nematic display applications.

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