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Nitrogen Containing Six-Membered Saturated Heterocycles as Structural Fragments In Liquid Crystals

Vladimir F. Petrov [a] & Assya I. Pavluchenko [b]

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

[b] Organic Intermediates & Dyes Institute, B. Sadovaya, 1/3, Moscow, 103787, Russia

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NITROGEN CONTAINING SIX-MEMBERED SATURATED HETEROCYCLES AS STRUCTURAL FRAGMENTS IN LIQUID CRYSTALS

Vladimir F. Petrov
LC Works, 6/68 Brinsley Road, Camberwell, VIC. 3124, Australia

Assya I. Pavluchenko
Organic Intermediates & Dyes Institute, B. Sadovaya, 1/3, Moscow 103787, Russia

The effect of the introduction of the 1,4-piperidine and 1,4-piperazine fragments into the molecular structure of liquid crystals on the appearance of the mesophases and their physico-chemical properties is discussed and compared with that of other well-known molecular fragments.

Keywords: piperidine derivatives; piperazine derivatives; physico-chemical properties; liquid crystals

INTRODUCTION

In continuation of our study of the structure-property relationships in nitrogen-containing liquid crystals [1–8] and saturated mesogens [9, 10], we present here our results on the study of the effect of the introduction of the 1,4-piperidine and 1,4-piperazine fragments into the molecular structure of liquid crystals on the appearance of the mesophases and their physico-chemical properties. The results of this study will be compared with those of the corresponding liquid crystals having other molecular fragments.

MESOMORPHIC PROPERTIES

1,4-Piperidine

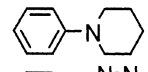
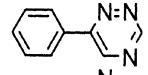
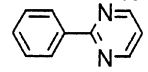
The phase transition temperatures of the 1,4-piperidine derivatives and the corresponding reference compounds are presented in Tables I–IV. The clearing points (nematic-isotropic or smectic-isotropic phase transition

TABLE I Mesomorphic Properties of Liquid Crystals: C_6H_{13} — A —  Z,

No.	A	Z	Phase transitions, °C	References
1-1		CN	Cr 30 N (13) I	[5]
1-2		CN	Cr 42 N 47 I	[11]
1-3		CN	Cr 48 N (42) I	[12]
1-4		CN	Cr 90 I	[13]
1-5		CN	Cr 73 N (17) I	[13]
1-6		CN	Cr 29 N 32.5 I	[1]
1-7		CN	Cr 52 Sm (26) I	[5]
1-8		CN	Cr 54.5 N (38.5) I	[14]
1-9		CN	Cr 77 I	[14]
1-10		CN	Cr 13.5 N 28 I	[15]
1-11		C_4H_9	Cr 20 SmB 44 I	[5]
1-12		C_4H_9	Cr-2.3 I	[16]
1-13		C_4H_9	Cr 33 SmB 40.5 I	[12]
1-14		C_4H_9	Cr 24.5 SmA 44 I	[17]
1-15		C_4H_9	Cr-2 SmE 40.5 SmB 48.5 I	[18]

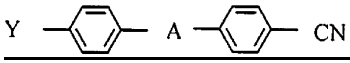
temperatures) of the 1,4-piperidine derivatives can be lower (compounds **1-1** and **1-2**, **1-3**, **1-5** to **1-8**, **1-10**; **1-11** and **1-15**; **2-1** and **2-2**, **2-7**, **2-9**; **2-12** and **2-13**, **2-14**; **3-1** and **3-2** to **3-7**; **3-8** and **3-9** to **3-14**; **4-1** and **4-2**) and higher (compounds **1-1** and **1-4**, **1-9**; **1-11** and **1-12**, **1-13**; **2-1** and **2-3** to **2-6**, **2-8**; **4-3** and **4-4**, **4-5**) and show the same values (compounds **1-11** and **1-14**) in comparison with those of the corresponding reference

TABLE II Mesomorphic Properties of Liquid Crystals: Y — A —  OC_4H_9

No.	Y	A	Phase transitions, °C	Ref.
2-1	C_6H_{13}		Cr 40 SmB 78 I	[5]
2-2	C_6H_{13}		Cr 20.8 Sm 54.5 SmA 83.4 I	[16]
2-3	C_6H_{13}		Cr 35.5 SmA 44 N 50 I	[12]
2-4	C_6H_{13}		Cr 55 N(44) I	[19]
2-5	C_6H_{13}		Cr 55 I	[19]
2-6	C_6H_{13}		Cr 50 Sm 54 N 61 I	[2]
2-7	C_6H_{13}		Cr 48 Sm 85 I	[2]
2-8	C_6H_{13}		Cr 40 N 53 I	[20]
2-9	C_6H_{13}		Cr 48 SmA 88 I	[17]
2-10	C_7H_{15}		Cr 40 I	[5]
2-11	C_8H_{17}		Cr 50 I	[5]
2-12	C_4H_9		Cr 70 SmB 132 I	[5]
2-13	C_4H_9		Cr 135 SmC 154 N 211 I	[21]
2-14	C_4H_9		Cr 90.3 SmH (73) SmG 113.7 SmC 120.7 SmA 215 I	[22]

compounds. Particularly, the low nematic thermostability of compound **4-5** can be explained by the predominance of the axial over equatorial conformation in the 1,4-silacyclohexane derivatives [36–38]. The melting temperatures (crystal-nematic or crystal-smectic or crystal-isotropic phase transition temperatures) of the 1,4-piperidine derivatives can be lower (compounds **1-1** and **1-2** to **1-5**, **1-7** to **1-9**; **1-11** and **1-13**, **1-14**; **2-1** and **2-4** to **2-7**, **2-9**; **3-1** and **3-2** to **3-7**; **3-8** and **3-9** to **3-12**, **3-14**) and higher (compounds **1-1** and **1-6**, **1-10**; **1-11** and **1-12**, **1-15**; **2-1** and **2-2**, **2-3**; **3-8**

TABLE III Physico-Chemical Properties of Liquid Crystals:

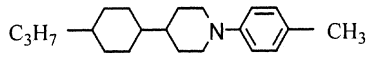
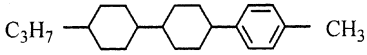
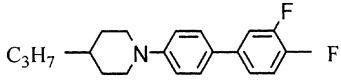
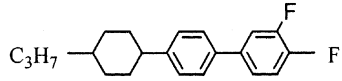
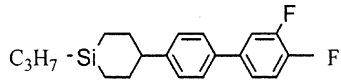
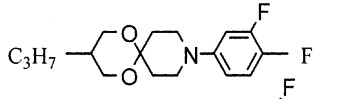
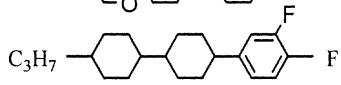
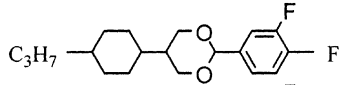
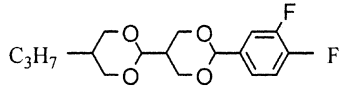
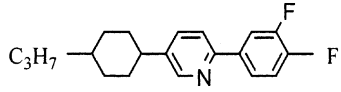
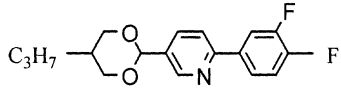
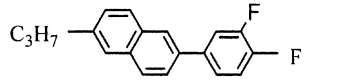


No.	Y	A	Phase transitions, °C	Δε	Ref.
3-1	C_4H_9O		Cr 86 N 106 I	34[a],14[b]	[5]
3-2	C_4H_9O		Cr 119 X 204 I		[23]
3-3	C_4H_9O		Cr 122 N 203 I		[12]
3-4	C_4H_9O		Cr 117 N 166 I		[24]
3-5	C_4H_9O		Cr 117 N 265 I		[4]
3-6	C_4H_9O		Cr_2 110 Cr_1 119 N 271.5 I		[25]
3-7	C_4H_9O		Cr 170 SmC 220 N 288 I		[21]
3-8	C_3H_7		Cr 119.1 I		[26]
3-9	C_3H_7		Cr 123 N 160 I		[23]
3-10	C_3H_7		Cr 128 N 180 I		[12]
3-11	C_3H_7		Cr 153.5 N 259 I		[25]
3-12	C_3H_7		Cr 167 N 278.5 I		[14]
3-13	C_3H_7		Cr 117.1 N (115.2) I		[24]
3-14	C_3H_7		Cr 182 N 257.5 I		[27]

X is an unknown mesophase.
[a]Extrapolated from the solution in the liquid crystal mixture at 20°C.
[b]$T_{meas} = 85°C$.

and **3-13**; **4-1** and **4-2**; **4-3** and **4-4**, **4-5**) and show the same values (compounds **2-1** and **2-8**) in comparison with those of the corresponding reference compounds. The introduction of the 1,4-piperidine fragment into

TABLE IV Physico-Chemical Properties of Some Liquid Crystals

No.		Phase transitions, °C	Δε	Δn	ν, mm^2s^{-1}	Ref.
4-1		Cr 91 SmB 125.4 SmA 127.9 N 161.6 I	9.7[a]	0.137[a]	29[b]	[26]
4-2		Cr 62 SmB 108 N 177 I	0.2[c]	0.111[c]	22[c]	[28]
4-3		Cr 112.9 SmA (106) N 117.5 I	13.7[a]	0.184[a]		[26]
4-4		Cr 66 N 102.4 I	10[c]	0.138[c]	31[c]	[28]
4-5		Cr 25.4 N 44 I				[29]
4-6		Cr 34.2 I	10.9[a]	0.103[a]	113.6[b]	[26]
4-7		Cr 46 N 124 I	5.5[d]	0.089[d]	21[d]	[30]
4-8		Cr 90 N 102.7 I	10.7[d]	0.092[d]		[31]
4-9		Cr 127.7 SmB 139.5 I				[32]
4-10		Cr 59.1 N 109.1 I				[33]
4-11		Cr 100.4 SmA 117.5 N 125 I				[34]
4-12		Cr 62 I	7.8[e]	0.200[e]		[35]

[a,b]Extrapolated from 15 wt% solution in the liquid crystal mixture at 25°C and 20°C, respectively.

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

[c]Extrapolated form 20 wt% solution in the liquid crystal mixture at 25°C.

the molecular core of liquid crystals results in the appearance (compounds **1-1** and **1-4**, **1-9**) and disappearance (compounds **2-1** and **2-3**, **2-4**, **2-6**, **2-8**; **2-12** and **2-13**; **3-8** and **3-9** to **3-14**) of the nematic phase. In the case of smectic phases, they appear (compounds **1-11** and **1-12**; **2-1** and **2-4**, **2-5**, **2-8**; **4-3** and **4-4**, **4-5**) and disappear (compounds **1-1** and **1-7**; **3-1** and **3-7**), and their number can be reduced (compounds **2-12** and **2-14**) in comparison with those of the corresponding reference compounds.

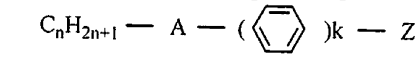
The importance of the position of the piperidine ring in the molecular core of liquid crystals can be illustrated by comparing the phase transition temperatures of compounds **2-1** and **2-10**, **2-11** (Table II), with nonmesomorphic behavior recorded for the latter derivatives. Their nonmesomorphism has been explained by the presence of about 11% of nonlinear (axial) conformers [5], while the linear equatorial conformers [39] can promote the formation of the mesophases in the 1,4-piperidine derivatives [5]. Both a geometric (increase of the content of equatorial conformer with respect to the N-Aryl bond) and an electronic (increase of the anisotropy of polarizability due to more extended conjugation) reasons have been used for the explanation of the mesomorphic properties in compound **2-1** [5]. It should be noted that previous work has proposed the absence of any significant amounts of nonchair conformers in simple piperidine and piperazine derivatives [40] as well as in the *trans*-1,4-cyclohexylene [41] and *trans*-1,3-dioxan-2,5-diyl [42] derivatives. Similar trends in the mesomorphic properties have been reported for other piperidine derivatives [43–47].

As evident from Table 4 and Tamura et al. [26], the spiro arrangement of the piperidine and dioxane rings results in the disappearance of the mesophases in comparison with those of the corresponding one- and two-fragment reference derivatives (compounds **4-6** and **4-3** to **4-5**; **4-7** to **4-11**), while the fused system **4-12** is also nonmesomorphic. Similar results have been reported for other spiro systems [26, 48, 49].

1,4-Piperazine

The phase transition temperatures of the 1,4-piperazine derivatives and the corresponding reference compounds are shown in Tables I, II and V–VII. As can be seen from Table I, the replacement of the 1,4-piperidine fragment by the 1,4-piperazine fragment in compound **1-11** to produce compound **1-12** results in the disappearance of the mesophase and lowers the melting point. Similar comparisons can be made with other reference compounds **1-13** to **1-15**, which exhibit smectic phases. While changing the terminal substituents and increasing the number of the phenylene fragments in the molecular core of the 1,4-piperazine derivatives can significantly affect their mesomorphic behavior and their thermal efficiency in comparison

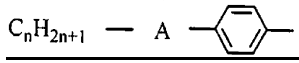
TABLE V Mesomorphic Properties of Liquid Crystals:



No.	n	A	k	Z	Phase transitions, °C	Ref.
5-1	5		1	CN	Cr 40 I	[50]
5-2	5		1	CN	Cr 30 N 55 I	[11]
5-3	5		1	CN	Cr 56 N (49) I	[12]
5-4	5		1	CN	Cr 98 I	[19]
5-5	5		1	CN	Cr 74 N (19) I	[19]
5-6	5		1	CN	Cr 33.6 N 43.5 I	[1]
5-7	5		1	CN	Cr 71 N (52) I	[14]
5-8	5		1	CN	Cr 87.5 I	[14]
5-9	4		2	CN	Cr 145.1 SmB 159.9 N 214.1 I	[51]
5-10	4		2	CN	Cr 120 N 202 I	[23]
5-11	4		2	CN	Cr 112 Sm 212.5 N 262 I	[25]
5-12	2		2	C_2H_5	Cr 174.3 SmB 193.8 I	[51]
5-13	2		2	C_2H_5	Cr 45.4 Cr_1 89.3 N 147 I	[52]
5-14	2		2	C_2H_5	Cr 228 I	[53]

with those of the corresponding reference compounds (it reveals the importance of the molecular structure of the 1,4-piperazine derivatives; see compounds **2-2** and **2-1**, **2-3** to **2-9**; **5-1** and **5-2** to **5-8**; **5-9** and **5-10**, **5-11**; **5-12** and **5-13**, **5-14**; **6-1** to **6-6** and **6-7** to **6-11**, **6-12** to **6-15**; **7-1** and **7-2** to **7-9**, Tables II, and V–VII). In some cases, the 1,4-piperazine derivatives show higher clearing (compounds **2-1** and **2-2**; **5-9** and **5-10**; **5-12** and **5-13**, **5-14**; **7-1** and **7-2**, **7-4**, **7-5**, **7-7**, **7-8**) and melting (compounds **5-1** and **5-2**, **5-6**; **5-9** and **5-10**, **5-11**; **5-12** and **5-13**) temperatures in

TABLE VI Physico-Chemical Properties of Liquid Crystals:

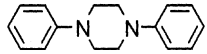
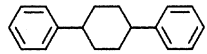
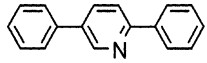
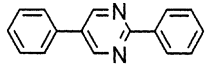
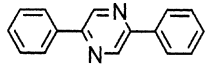
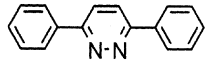
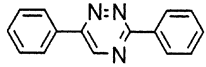
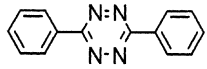
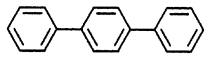
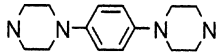
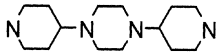
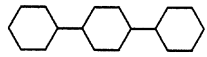


No.	n	A	Phase transitions, °C	d, Å	d/L	Reference
6-1	4		Cr 61.1 SmA (57.7) N 113.8 I	25.4[a]	1.37[a]	[50]
6-2	5		Cr 61.8 SmA 93.3 N 122.2 I			[50]
6-3	6		Cr 79.7 SmA 113 N 120.6 I			[50]
6-4	7		Cr 70.2 SmA 125 I			[50]
6-5	8		Cr 59.3 SmA 127.4 I	31.8[b]	1.38[b]	[50]
6-6	9		Cr 55 SmA 131 I			[50]
6-7	4		Cr 57 SmA_d (32) N 144 I			[54]
6-8	5		Cr 49 SmA_d 61 N 149.5 I			[54]
6-9	6		Cr 54 SmA_d 106 N 144 I			[54]
6-10	7		Cr 39 SmA_d 120 N 143.5 I			[54]
6-11	8		Cr 48 SmA_d 128 N 137.5 I	34.2	1.35	[54]
6-12	4		Cr 73.5 N 150.2 I			[3]
6-13	5		Cr 65.7 N 155.1 I			[3]
6-14	6		Cr 32.1 Sm 123.1 N 146.2 I			[3]
6-15	7		Cr 48 Sm 133 N 143 I			[3]

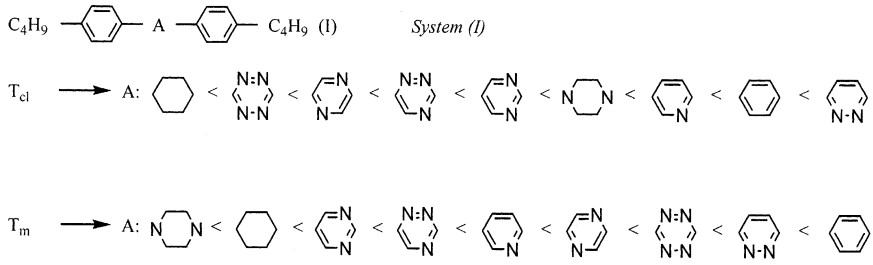
[a] $T_{meas} = 50°C$.
[b] $T_{meas} = 75°C$.

comparison with those of the corresponding reference compounds. The replacement of the 1,4-piperazine by the *trans*-1,4-cyclohexylene and pyridin-2,5-diyl in compounds **6-1** to **6-5** to obtain compounds **6-7** to **6-11** and **6-12** to **6-15**, respectively, increases the clearing points and changes their ascending behavior to the descending ones. The 1,4-piperazine derivatives exhibit more pronounced appearance of the smectic phases (compounds **6-1**, **6-2** and **6-12**, **6-13**; **6-4**, **6-5** and **6-10**, **6-11**). The ratio

TABLE VII Mesomorphic Properties of Some Liquid Crystals:
C_4H_9 — A — B — K — C_4H_9

No.	A--B--K	Phase transitions, °C	Reference
7-1		Cr 57 Sm 119 Sm 190 I	[55]
7-2		Cr 89 Sm 107 I	[55]
7-3		Cr 161 Sm 198 I	[23]
7-4		Cr 118 SmA 186 I	[56]
7-5		Cr 161.3 SmC 166.4 N 181.9 I	[57]
7-6		Cr 205 Sm 213 N 219 I	[23]
7-7		Cr 155 N 182 I	[21]
7-8		Cr 170 N 172 I	[58]
7-9		Cr 208 Sm 218 I	[53]
7-10		Cr 36.3 SmE 106.9 Sm 113.4 SmB 179.5 I	[16]
7-11		Cr 68 SmB 182 I	[23]
7-12		Cr 104 Sm 265 I	[55]

d/L characterizing the molecular overlap in the formation of the dimers (d is the layer spacing defined from X-ray diffraction measurements, L is the molecular length) shows very similar values for the corresponding 1,4-piperazine derivative **6-5** and the *trans*-1,4-cyclohexylene derivative **6-11**, while X-ray diffraction study of three-ring weakly polar 1,4-piperazine derivatives reveals the monolayer arrangement of their smectic phases [59, 60]. The efficiency of the 1,4-piperazine fragment introduced into the molecular core of the system (1) can be characterized by the following orders of increasing the clearing points T_{cl} and melting temperatures T_m (compounds **7-1** to **7-9**, Table VII):



SYSTEM (I).

These results reveal that the introduction of the 1,4-piperazine fragment into the molecular core of the system (1) produces liquid crystals exhibiting the lowest melting points and moderate clearing temperatures among compounds of this system.

It is evident from Table VII that the introduction of two 1,4-piperazine fragments into the molecular core of three-ring derivatives significantly lowers the clearing and melting points and increases the number of the smectic phases in comparison with those of the corresponding terphenylene derivative (compounds **7-9** and **7-10**). The suppressed phased transition temperatures have been recorded for compound **7-11** containing two 1,4-piperidine and one 1,4-piperazine fragments (compare with those of the tercyclohexylene derivative **7-12**). Similar trends have been observed for other 1,4-piperazine derivatives [59–67].

As in the case of the 1,4-piperidine derivatives, the existence of the mixtures of few conformers [39] and their contents influence the formation of the mesophases in the 1,4-piperazine derivatives [16, 60]. The predominance of the equatorial, equatorial disubstituted chair form of the conformer with a linear structure in these mixtures is important for the formation of the mesophases. Otherwise, it leads to the disappearance of the liquid crystalline properties (compounds **1-2**, **5-1**, Tables I, V) [16].

We can propose that the electronic and geometrical structure of the 1,4-piperidine [68, 69] and 1,4-piperazine [70, 71] play a very important role in the intra- and inter-molecular interactions [72–74] which affect the packing of the molecules which predominantly influence mesophase stability [72–76]. Anisotropatic dispersion interactions, and consequently the anisotropy of polarizability (which is higher for the piperidine in comparison with that of the cyclohexane [77–78], depending on the electron density distribution in the molecular fragments under consideration, also influence the packing and hence the stability of the mesophases but play a secondary role compared to the steric factors [76]. Other molecular aspects such as the association [75] or dipole-dipole attraction in polar liquid crystalline

derivatives which can influence the packing of the molecules also affect the stability of the mesophases [76].

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 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 [79]:

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

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

The data presented in Table IV reveals that the replacement of the *trans*-1,4-cyclohexylene ($\mu = 0$ [80]) by the 1,4-piperidine ($\mu = 1.16$D [81]) significantly increases the dielectric anisotropy (compounds **4-1** and **4-2**; **4-3** and **4-4**) due to the total dipole moment and molecular polarizability [77, 78] being increased (see also compound **3-1**, Table III and Adomenas and Sirutkaitis [46]). The dipole moment of the 1,4-piperazine is 1.47D [81], which correspondingly contributes to the total molecular dipole moments of some three-ring nitro derivatives, resulting in their dielectric anisotropy of 12–16 [61].

It is understandable that the purpose of the spiro arrangement of the dioxan and piperidine rings could be the formation of a new molecular fragment exhibiting a higher dipole moment than that of other well-known molecular fragments, for example, the *trans*-1,4-cyclohexylenes. And this purpose was successfully achieved; compare the dielectric anisotropy of compounds **4-6** and **4-7**, **4-8**, **4-12**.

OPTICAL PROPERTIES

The phenomenological relation between the refractive index and the electric polarization is defined as [82, 83]

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

where the mean polarizability $\alpha^* = (\alpha_{\parallel} + 2\alpha_{\perp})/3$, the mean refractive index $\mathrm{n}^{*^2} = (\mathrm{n}_{\mathrm{e}}^2 + 2\mathrm{n}_{\mathrm{o}}^2)/3$, and n_{o} is the ordinary and n_{e} the extraordinary refractive indices. From Equation (2) and previous paragraph, it follows that the 1,4-piperidine derivatives which have a larger induced polarizability of their highly conjugated π-electron system [77, 78] exhibit the

optical anisotropy $\Delta n = n_e - n_o$ which is much larger than that of the corresponding *trans*-1,4-cyclohexylene derivatives (compounds **4-1** and **4-2**, **4-3** and **4-4**). Similar conclusions can be derived for the spiro system **4-6** in comparison with the reference compounds **4-7**, **4-8**, while the fused aromatic system **4-12** exhibits the highest value of the optical anisotropy among these derivatives (as expected).

VISCOUS PROPERTIES

It has been shown that the nematic liquid crystalline materials for display applications should have a low viscosity for giving the acceptable response times to Liquid Crystal Displays [84, 85]. According to the results on the kinematic viscosity ν presented in Table IV, the replacement of the *trans*-1,4-cyclohexylenes by the saturated heterocyclic fragments and spiro systems increases the viscosity (compounds **4-1** and **4-2**, **4-6** and **4-7**). These results can be expected, considering the fact that the introduction of the heteroatom into the aromatic and saturated systems, an increase in the size of the molecular fragments, and a spiro arrangement usually increase the viscosity of the corresponding liquid crystals [6, 9, 10, 49].

CONCLUSION

Systematic studies on the introduction of the nitrogen-containing six-membered saturated heterocycles and the spiro systems on their basis into the molecular structure of liquid crystals on the creation of the mesophases and their physico-chemical properties have been performed, with attempts to correlate the molecular level parameters with the observed properties. The information presented here may lead to a better understanding of the nature of liquid crystals.

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