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Furan as a Structural Fragment in Liquid Crystals

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FURAN AS A STRUCTURAL FRAGMENT IN LIQUID CRYSTALS

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The effect of the introduction of the furan and furan-based systems 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: furan; physico-chemical properties; liquid crystals

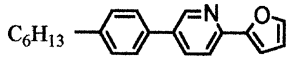
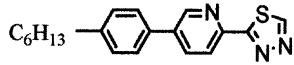
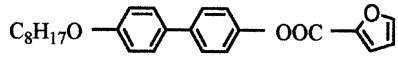
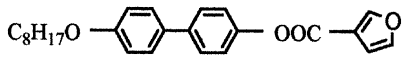
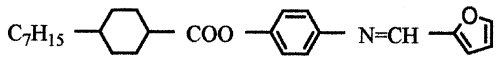
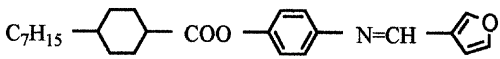
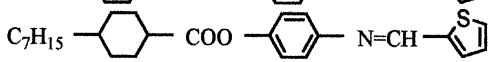
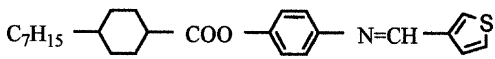
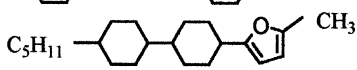
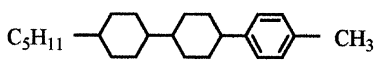
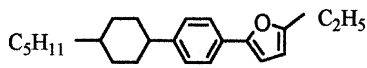
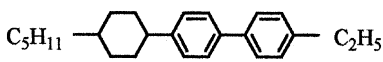
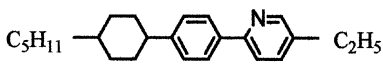
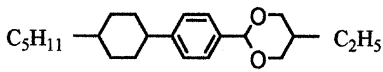
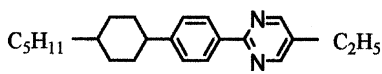
INTRODUCTION

In continuation of our study of the structure-property relationships in the oxygen-containing liquid crystals (see, for example, our previous publications [1–3]), we present here our results on the study of the effect of the introduction of the furan and furan-based systems 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

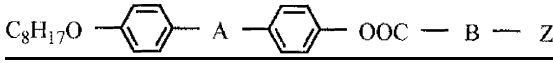
It has been reported that the introduction of furan [4–8] into the molecular core of two-ring derivatives does not produce mesophases. Their non mesomorphic behavior has been explained in terms of their significant molecular nonlinearity [9]. Mesophases can be observed in three-ring furan derivatives presented in Tables I and II. Their decreased mesomorphic

TABLE I Mesomorphic Properties of Some Liquid Crystals

No.	Compound	Phase transitions, °C	Ref.
1-1		Cr 55 Sm 103 I	[10]
1-2		Cr 82 Sm 128 I	[11]
1-3		Cr 96 SmG (86.7) Sm (87.6) N 110.8 I	[12]
1-4		Cr 116 SmE 116.8 SmB 123.1 N 131.2 I	[12]
1-5		Cr 110 N (106) I	[13]
1-6		Cr 105 N 143 I	[13]
1-7		Cr 109 N 138 I	[13]
1-8		Cr 99 N 145 I	[13]
1-9		Cr 15.3 SmB 87.1 I	[14]
1-10		Cr 55.8 Sm 138 N 178.6 I	[15]
1-11		SmA 52 N 60 I	[14]
1-12		Cr 34 Sm 146 N 164 I	[16]
1-13		Cr 65.8 Sm 78 N 168 I	[17]
1-14		Cr 73.3 N 136.3 I	[18]
1-15		Cr 116 N 178 I	[19]

stability in comparison with that of the corresponding reference compounds (compounds **1-1** and **1-2**, **1-5** and **1-7**, **1-6** and **1-8**, **1-9** and **1-10**, **1-11** and **1-12** to **1-15**, **2-1** and **2-2**, **2-3** and **2-4**, **2-5** and **2-6**, **2-7** and **2-8**, Tables I and II) has been rationalized in terms of their increased molecular

TABLE II Mesomorphic Properties of Liquid Crystals:



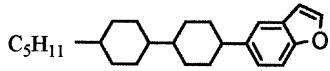
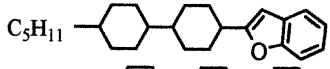
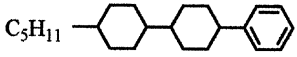
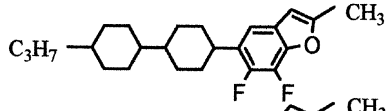
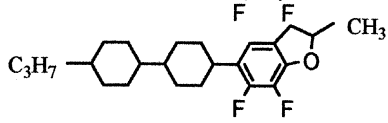
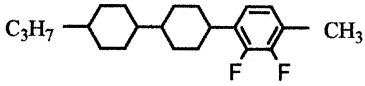
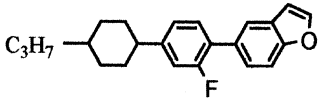
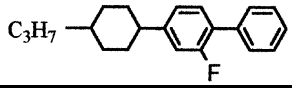
No.	A	B	Z	Phase transitions, °C	Ref.
2-1	OOC		CN	Cr 134.9 SmA_2 140.2 SmA_d 140.5 N 147.4 I	[20]
2-2	OOC		CN	Cr 129 SmA_d 199 N 241 I	[21]
2-3	OOC		Br	Cr 118.3 N 122.1 I	[22]
2-4	OOC		Br	Cr 128 SmA 192 N 222 I	[23]
2-5	OOC		NO_2	Cr 139 SmA_2 (132.7) SmA_d 164.7 N 172.6 I	[24]
2-6	OOC		NO_2	Cr 101 SmA 109 SmA 129 N 228 I	[23]
2-7	COO		NO_2	Cr 157.2 SmA_d 160.4 N 173.1 I	[24]
2-8	COO		NO_2	Cr 165 SmA 239 N 246 I	[23]

nonlinearity [9, 22] and decreased anisotropy of polarizability [13, 25]. The enhanced clearing temperatures of 3-furanyl systems with respect to those of the corresponding 2-furanyl systems (compounds **1-3** and **1-4**, **1-5** and **1-6**, Table I) have been explained in terms of increased anisotropy of molecular polarizability [12, 13] and decreased molecular nonlinearity [12]. Similar results have been reported for the thienyl systems (compounds **1-7** and **1-8**, Table I, Brown et al. [12], Nugent et al. [13]). The melting temperatures of the furan derivatives can be lower (compounds **1-1** and **1-2**, **1-9** and **1-10**, **2-3** and **2-4**, **2-7** and **2-8**, Tables I and II) and higher (compounds **1-5** and **1-7**, **1-6** and **1-8**, **2-1** and **2-2**, **2-5** and **2-6**) than those of the corresponding reference compounds Similarly, 3-furanyl systems exhibit higher (compounds **1-3** and **1-4**) and lower (compounds **1-5** and **1-6**) melting points with respect to those of the corresponding 2-furanyl systems. The nematic ranges of the furan derivatives can be narrower (compounds **1-6** and **1-8**, **1-11** and **1-12** to **1-15**, **2-1** and **2-2**, **2-3** and **2-4**, **2-5** and **2-6**) and wider (compounds **2-7** and **2-8**) in comparison with those of the corresponding reference derivatives. Similarly, 3-furanyl systems show wider (compounds **1-5** and **1-6**) and narrower (compounds **1-3** and **1-4**) nematic ranges in comparison with those of the corresponding 2-furanyl systems. In some cases, the introduction of the furan into the molecular structure of three-ring derivatives results in the disappearance of the

nematic phase (compounds **1-9** and **1-10**, Table I), smectic phase (compounds **2-3** and **2-4**, Table II), and re-entrant nematic phase [22] in comparison with those of the corresponding reference derivatives. Aslo, furan can introduce the smectic phase (compounds **1-11** and **1-14**, **1-15**) and can form only smectic phase (compounds **1-1**, **1-9**). Similar trends have been observed for other furan derivatives [25–34].

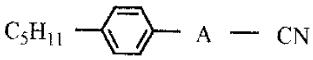
It is well known that the fusion of two rings can produce molecular fragments that in some cases show a higher mesomorphic stability in comparison with that of each of these two rings [3, 35, 36]. The fusion of the furan and benzene rings gives the 1-benzofuran [8, 37–39], which can be used as a structural fragment in liquid crystals presented in Tables III and IV. It is evident from Tables 3 and 4 and that 1-benzofuran derivatives exhibit higher (compounds **3-1**, **3-2** and **3-3**; **3-4** and **3-6**; **3-7** and **3-8**; **4-1**, **4-2** and **4-3**; **4-9** and **4-11**) and lower (compounds **4-10** and **4-11**) clearing points with respect to those of the corresponding phenylene derivatives. Comparing with other reference derivatives, the 1-benzofuran derivatives

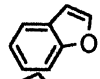
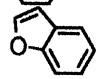
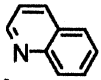
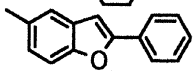
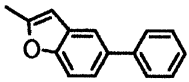
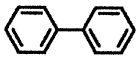
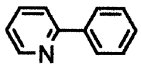
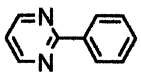
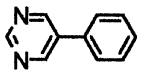
TABLE III Physico-Chemical Properties of Some Liquid Crystals

No.	Compound	Phase transitions, °C	$\Delta\varepsilon$	Δn^a	Ref.
3-1		Cr 80 SmB 110 N 158 I	0.83[a]	0.108	[40]
3-2		Cr 95 SmB 96 N 166.7 I			[41]
3-3		Cr 61.6 Sm 107.9 N 111.8 I			[15]
3-4		Cr 89 N 173.6 I	−5.40[b]	0.117	[42]
3-5		Cr 112 N (105.1) I	−6.70[b]	0.073	[42]
3-6		Cr 67 N 145.3 I	−2.80[b]	0.095	[43]
3-7		Cr 86 N 99.6 I	1.94[a]	0.165	[40]
3-8		Cr 70 I			[44]

[a,b]Extrapolated from 10 wt% solution in ZLI-4792 and ZLI-2857 at 20°C, respectively.

TABLE IV Physico-Chemical Properties of Some Liquid Crystals:



No.	A	Phase transitions, °C	Δε	Δn	Reference
4-1		Cr 51.1 N 56.4 I	8.05[a]	0.170[b]	[45]
4-2		Cr 99.7 N (86.5) I			[45]
4-3		Cr 22.5 N 35 I	13.3[c]	0.178[c]	[46, 47]
4-4		Cr 73 I	17.9[d]	0.204[d]	[48]
4-5		Cr 47.4 N 68 I	6.5[e]	0.205[f]	[48–50]
4-6		Cr 108.5 I			[51]
4-7		Cr 96 N 109 I			[51]
4-8		Cr 91.8 N 135.5 I			[52]
4-9		Cr 139 N 252.6 I			[45]
4-10		Cr 133.8 N 230.5 I			[45]
4-11		Cr 130 N 239 I			[46]
4-12		Cr 76 N 232.1 I			[48]
4-13		Cr 125 N 241 I			[53]
4-14		Cr 131.5 Sm 176 N 261.5 I			[53]

[a,b]Extrapolated from 22 wt% solution in the liquid crystal material at 20°C and 25°C, respectively.

[c]$\tau = T_{meas}/T_{N\text{-}I} = 0.96$; T_{meas}, $T_{N\text{-}I}$, K.

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

[e]$\tau = 0.95$.

[f]$\tau = 0.94$.

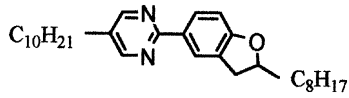
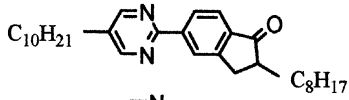
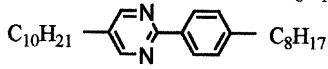
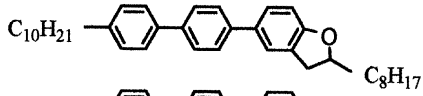
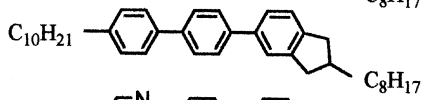
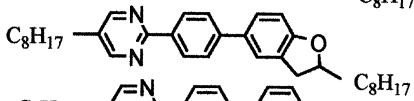
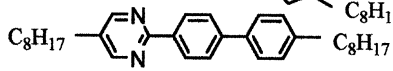
show a higher (compounds **4-1** and **4-4**, **4-6**; **4-2** and **4-4** to **4-6**; **4-9** and **4-12**, **4-13**) and a lower (compounds **4-1**, **4-2** and **4-7**, **4-8**; **4-9** and **4-14**; **4-10** and **4-11** to **4-14**) nematic thermostability. The melting temperatures of the 1-benzofuran derivatives can be higher (compounds **3-1**, **3-2** and **3-3**; **3-4** and **3-6**; **3-7** and **3-8**; **4-1** and **4-3**, **4-5**; **4-2** and **4-3** to **4-5**, **4-7**, **4-8**; **4-9**, **4-10** and **4-11** to **4-14**) and lower (compounds **4-1** and **4-4**, **4-6** to **4-8**; **4-2** and **4-6**) than those of the corresponding reference compounds. Similarly, the nematic ranges of the 1-benzofuran derivatives can be wider (compounds **3-1**, **3-2** and **3-3**; **3-4** and **3-6**; **3-7** and **3-8**; **4-1** and **4-4**, **4-6**; **4-9** and **4-11**, **4-14**; **4-10** and **4-14**) and narrower (compounds **4-1**, **4-2** and **4-3**, **4-5**, **4-7**, **4-8**; **4-9** and **4-12**, **4-13**; **4-10** and **4-11** to **4-13**) in comparison with those of the corresponding reference compounds.

This consideration reveals the importance of the position of the 1-benzofuran fragment in the molecular core of liquid crystals (which can lead to the different molecular nonlinearity [54]), resulting in the higher clearing and melting temperatures of compounds having the oxygen of the 1-benzofuran pointed towards the weakly polar part of the molecular core (compounds **3-1** and **3-2**, **4-1** and **4-2**) and towards the strong polar part (compounds **4-9** and **4-10**). Similarly, the nematic ranges can be wider for the 1-benzofurans with its oxygen pointed towards the weakly polar part of the molecular core (compounds **3-1** and **3-2**) and toward the strong polar part (compounds **4-1** and **4-2**, **4-9** and **4-10**). These findings also reveal the influence of the molecular structure of the 1-benzofuran-2,5-diyl derivatives on their mesomorphic properties.

Interestingly, the positions of oxygen atoms in the 1-benzofuran-2,5-diyl fragment and nitrogen atoms in the heterocycles of the corresponding reference compounds presented in Table IV show similar influence on their mesomorphic thermostability (compare compounds **4-1** and **4-2**, **4-4** and **4-5**, **4-6** and **4-7**; **4-9** and **4-10**, **4-13** and **4-14**). Similar trends have been observed for other 1-benzofuran-2,5-diyl derivatives [54, 55].

In the meantime, it has been shown that the tetrahydrofuran derivatives exhibit very low mesomorphic stability [56–60], and in some other cases they are not mesomorphic at all [56–57]. It is evident from Tables III and V that the liquid crystals containing 2,3-dihydro-benzofuran-2,5-diyl fragment (which is a result of the fusion of the benzene and tetrahydrofuran [61–63] rings) exhibit lower clearing temperatures and higher melting points (compounds **3-5** and **3-6**, **5-1** and **5-3**, **5-6** and **5-7**) and a reduced number of the mesophases (compounds **5-1**, and **5-3**, **5-6** and **5-7**) with respect to those of the corresponding 1,4-phenylene derivatives. The corresponding 2,5-disubstituted indan derivative **5-5** shows lower smectic A phase thermostability and melting point and a lower number of the mesophases in comparison with those of the 2,5-disubstituted 2,3-dihydro-benzofuran derivative **5-4**. Interestingly, the carbonyl group, working as a

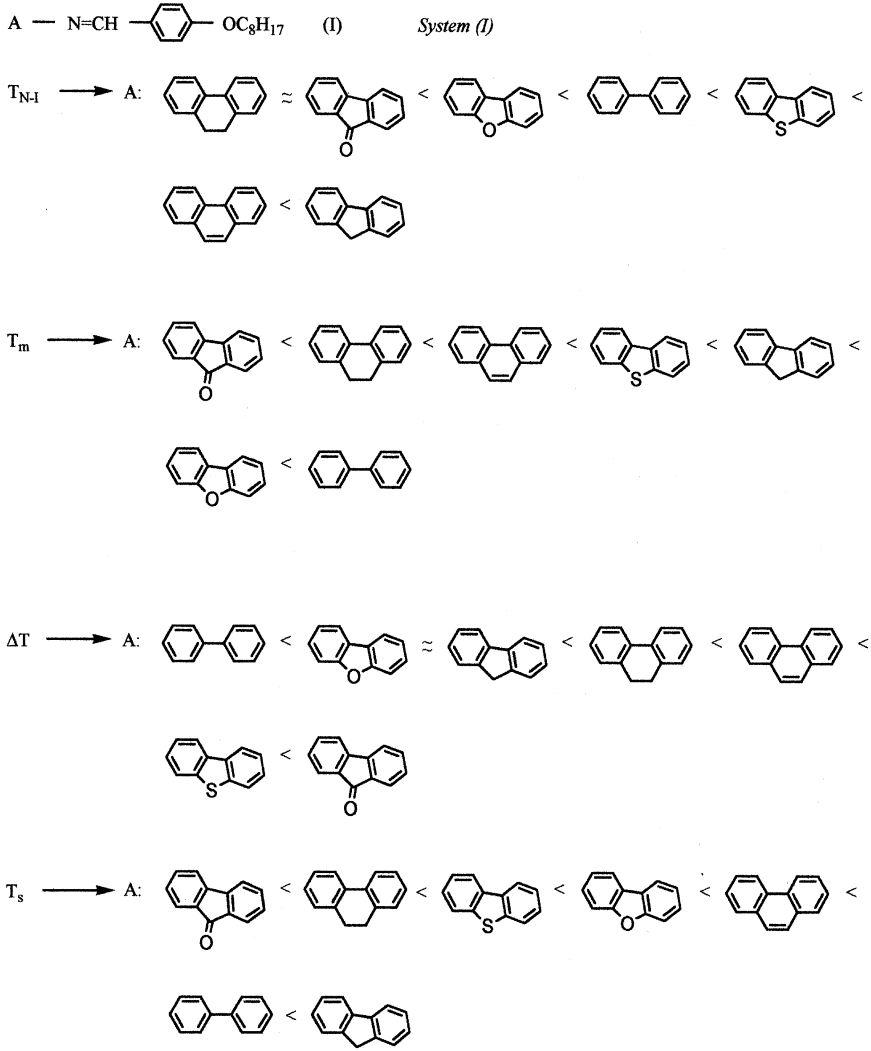
TABLE V Mesomorphic Properties of Some Liquid Crystals

No.	Compound	Phase transitions, °C	Ref.
5-1		Cr 50.2 SmA (46.9) I	[64]
5-2		Cr 83 I	[65]
5-3		Cr 33.6 SmF 36.7 SmC 46.2 SmA 59.8 I	[66]
5-4		Cr 106.7 SmC (51.2) Sm 105.8 Sm 131.5 SmA 174.3 I	[64]
5-5		Cr 97 Sm 119 SmC 126 SmA 159 I	[67]
5-6		Cr 81.3 SmC 103.6 N 140 I	[64]
5-7		Cr 72.3 SmC 130.2 SmA 145.2 N 152.5 I	[68]

lateral substitutent [69] in compound **5-2**, does not produce a mesophase (compared with that of compound **5-1**, which contains a cyclic ether oxygen).

One more example of the liquid crystals having furan-based systems is compound **6-1**, which contains dibenzofuran fragment [70–77] (Table VI). It should be noted that the corresponding biphenylene derivative **6-7** exhibits higher melting and clearing temperatures and a higher smectic thermostability. As discussed before, the carbonyl group in compound **6-2** works as a lateral substituent [69], reducing the smectic and nematic thermostabilities in comparison with those of the parent compound **6-5** and 3-dibenzofuran derivative **6-1** as well. As evident from Table VI, the presence of oxygen atom in the 3-dibenzofuran derivative **6-1** results in a lowering of the nematic phase and smectic A phase thermostabilities and in a slight increase of the melting point in comparison with the those of the parent compound **6-4**. The influence of the introduction of the fragment A into the molecular core of compounds presented in Table VI on their mesomorphic properties can be expressed by the following orders of increasing nematic-isotropic phase transition temperatures, ($T_{N\text{-}I}$), melting temperatures

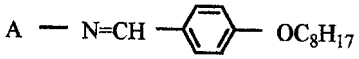
(crystal-smectic or crystal-nematic phase transition temperatures, T_m), nematic ranges (ΔT), and smectic thermostabilities (smectic-nematic phase transition temperatures, T_s):

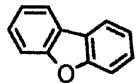
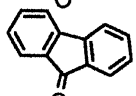
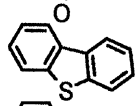
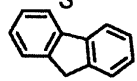
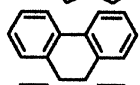
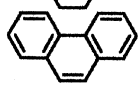
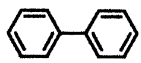


LIST OF SYSTEMS: System (I).

These results reveal that the introduction of the dibenzofuran fragment into the molecular core of the system (I) results in the formation of liquid crystals exhibiting the mesophases with moderate nematic and smectic

TABLE VI Mesomorphic Properties of Liquid Crystals:



No.	A	Phase transitions, °C	Ref.
6-1		Cr 118.5 SmA 128.5 N 152.5 I	[78]
6-2		Cr 86 Sm (70) N 142 I	[79]
6-3		Cr 115 SmA 119.4 N 170 I	[78]
6-4		Cr 117.5 SmA 165.5 N 189.5 I	[79]
6-5		Cr 98 SmA (78) N 142 I	[80]
6-6		Cr 103 Sm 140 N 186.5 I	[81]
6-7		Cr 142.5 Sm 155.5 N 164 I	[79]

thermostabilities, high melting point, and narrow nematic range among the compounds of the system (I).

It is believed that the electronic and geometrical structure of the furan [4–8] and furan-based systems [8, 37–39, 70–77] play a very important role in the intra-and inter-molecular interactions [82–84] that affect the packing of the molecules which predominantly influence mesophase stability [82–86]. Anisotropic dispersion interactions, and consequently the anisotropy of polarizability, which depend 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 [86]. Other molecular aspects such as the association [85] or dipole-dipole attraction in polar liquid crystalline derivatives which can influence the packing of the molecules also affect the stability of the mesophases [86].

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 [87];

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

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 Tables III and IV reveal that more pronounced contribution to the perpendicular component of the molecular dipole moment of the dipole structure of the 1-benzofuran-2,5-diyl and 2,3-dihydro-benzofuran-2,5-diyl fragments lowers the dielectric anisotropy of these derivatives in comparison with that of the corresponding reference compounds (compounds **3-4**, **3-5** and **3-6**; **4-1** and **4-3**, **4-4**). Compound **4-5** exhibits a similar decrease in the dielectric anisotropy owing to the position of the nitrogen of its pyridine ring. Similar trends have been recorded for other 1-benzofuran-2,5-diyl derivatives [40,45].

OPTICAL PROPERTIES

The phenomenological relation between the refractive index and the electric polarization is defined as [88, 89].

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

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 the previous paragraph, it follows that the 1-benzofuran-2,5-diyl derivatives which have a larger induced polarizability of their highly conjugated π-electron system exhibit the optical anisotropy $\Delta\mathrm{n} = \mathrm{n}_\mathrm{e} - \mathrm{n}_\mathrm{O}$, which is much larger than that of the corresponding 2,3-dihydro-benzofuran-2,5-diyl derivatives and parent compounds (compounds **3-4** and **3-5**, **3-6**) and is similar to that of other highly polarizable aromatic and heteroaromatic reference compounds (compounds **4-1** and **4-3** to **4-5**). Similar results have been found for other liquid crystalline 1-benzofurans (compound **3-7**, Table III, Kirsch et al. [40] and Goodby et al. [45]).

CONCLUSION

Systematic studies on the introduction of the furan and furan-based systems 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 here presented may lead to a better understanding of the nature of liquid crystals.

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