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Cyclic Esters as Structural Fragments in Liquid Crystals

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The effect on the physicochemical and electro-optical properties of introducing cyclic esters into the molecular structure of liquid crystals is discussed and rationalized in terms of existent theories.

Keywords: cyclic esters; electro-optical properties; liquid crystals; physicochemical properties

1. INTRODUCTION

This review focuses on the effect of introducing the fragments containing ester groups into the molecular structure of liquid crystals on their physicochemical and electro-optical properties. It is believed that the charasteristic effects of cyclic esters can be correlated with the geometric and electronic structures of the ester groups [1].

2. MESOMORPHIC PROPERTIES

The phase-transition temperatures of some cyclic esters and reference compounds are presented in Tables 1–4, where Cr, Sm, SmB, SmC*, SmA, N, N_{RE}, Ch, BP, and I denote the crystalline, smectic, smectic B, chiral smectic C*, smectic A, nematic, reentrant nematic, cholesteric, blue phase, and isotropic phases, respectively. Values given in parentheses refer to monotropic phase transitions.

As is evident from Table 1, the introduction of a chiral 2-oxetanone unit [2,3], in which the competition between classical ring strain forces and torsional forces caused by interaction of atoms out of the ring tends to bend the ring, forms some monotropic phases with high melting points (crystal–smectic or crystal–nematic phase-transition

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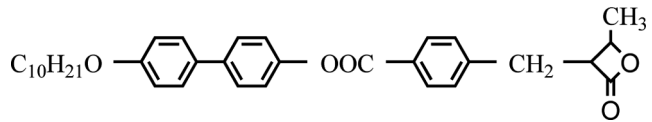
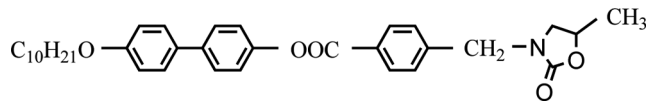
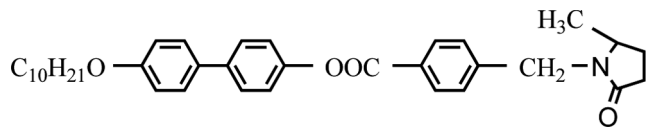
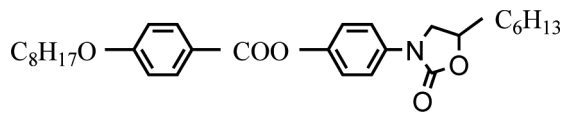
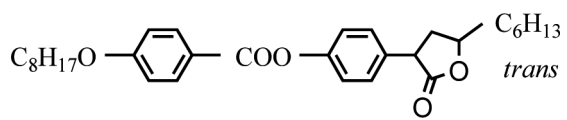
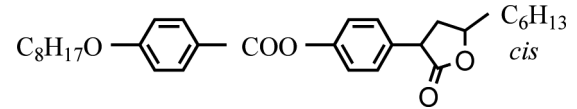
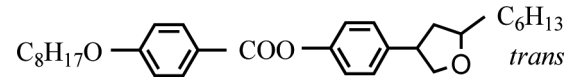
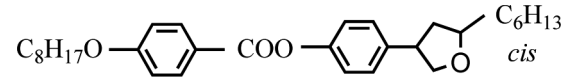
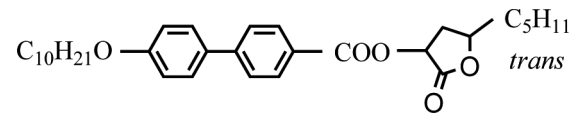
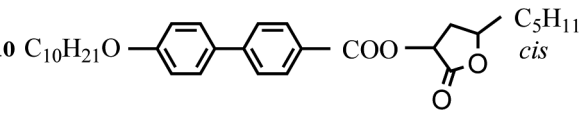
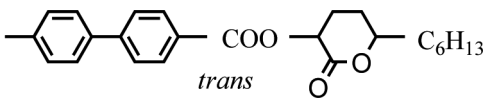
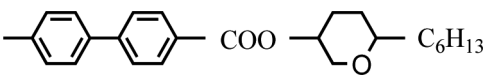
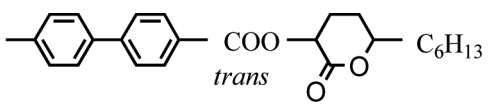
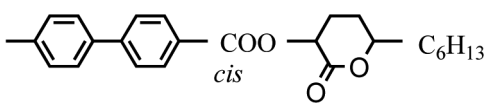
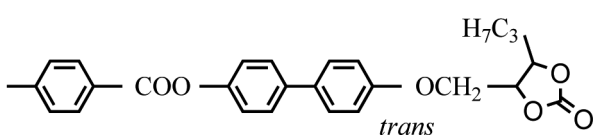
TABLE 1 Physicochemical and Electro-optical Properties of Liquid Crystals

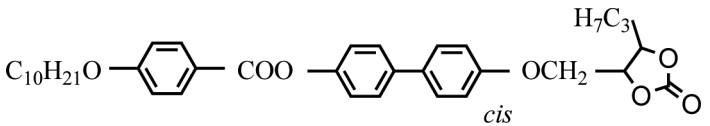
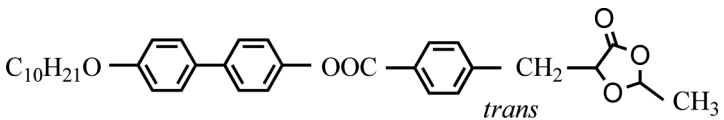
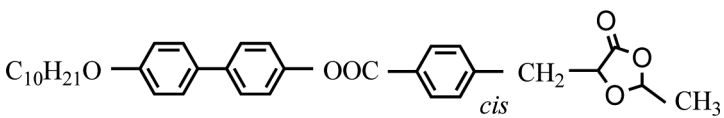
No.	Compound	Phase transitions (°C)	$\lvert P_s \rvert$(nCcm^{-2})	τ(μs)	θ (deg)	Ref.
1-1		Cr 159 SmA (148) Ch (152) BP (153) I	10.5[a]	1.1[b]		4
1-2		Cr 1831				5
1-3		Cr 122 SmC* 134 I				5
1-4		Cr 109 Sm 147 I	7.7[c]	235[c]	21[c]	6
1-5	 *trans*	Cr 103 I	~0[d]	891[d]	14[d]	6,7

1-6	 *cis*	Cr 971	12.5[e] 14.5[c]	98[e] 119[c], 162[g]	24[e] 25[c]	6,7
1-7	 *trans*	Cr 59 SmB 87.5 SmA 95 I	~ 0[f]	slow[f]		7
1-8	 *cis*	Cr 57 SmB (33) SmA 61 I	4.7[f]	150[f]		7
1-9	 *trans*	Cr 119 I	1.2[k]	229[k]	18[k]	8
1-10	 *cis*	Cr 142 I	4.9[k]	82[k]	20[k]	8

[a,b]Measured in 9.24 mol% solution in liquid-crystalline material (LCM) at 105 and 120°C, respectively.
[c]Measured in 5 wt% solution in LCM I at 25°C.
[d,f]Measured at 25°C.in 10 wt% solution in LCM II and LCM III, respectively.
[e]Measured in 4 wt% solution in LCM II at 25°C.
[g]Measured in 2 wt% in LCM III at 25°C.
[k]Measured in 2 mol% solution in LCM IV at 25°C.

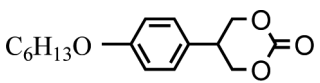
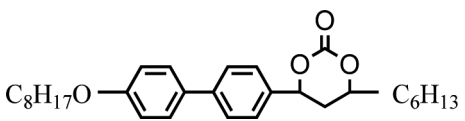
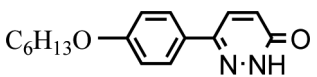
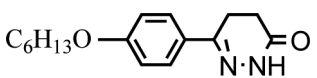
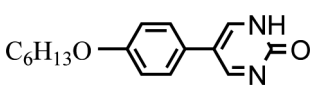
TABLE 2 Physicochemical and Electro-optical Properties of Some Liquid Crystals

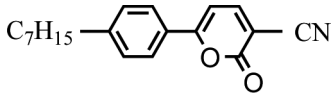
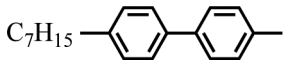
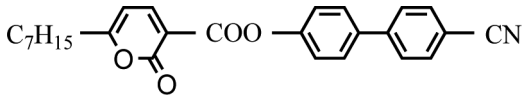
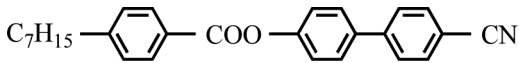
No.	Compound	Phase transitions (°C)	$\lvert P_s \rvert$(nCcm^{-2})	τ(μs)	θ (deg)	Ref.
2-1	 *trans*	Cr 107 SmC* 131 I	2.5[a]	137[a]	19[a]	16
2-2		Cr 99.8 SmC* (89.1) SmA 134.6 Ch 136.1 I				17
2-3	 *trans*	Cr 111 SmC* 128 I	2.4[b] 350[c]	195[b]	21[b]	18
2-4	 *cis*	Cr 152 I	4.2[b]	126[b]	22.3[b]	18
2-5	 *trans*	Cr 133.5 SmA 146.5 I	2[d]			19

2-6	 *cis*	Cr 122.5 I	4.9[d]			19
2-7	 *trans*	Cr 71 SmC* 75 Ch 85 I	64[e]	150[e]	35[e]	20
2-8	 *cis*	Cr 103 I	181[f]			20

[a]Measured in 2 wt% solution in LCM V 25°C.
[b]Measured in 2 mol% solution in LCM VI at 25°C.
[c]$T_{meas} =$ 105°C.
[d]Measured in 7.2 mol% solution in LCM VII at 50°C.
[e]Measured in SmC* phase.
[f]Measured in 10 mol% solution in LCM VIII at 25°C.

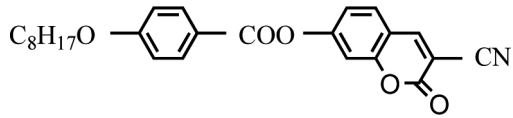
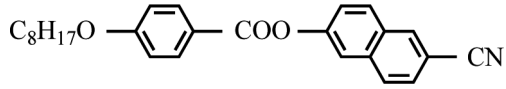
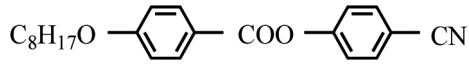
TABLE 3 Physicochemical Properties of Some Liquid Crystals

No.	Compound	Phase transitions (°C)	$\Delta\varepsilon$	Reference
3-1		Cr 61 SmA (39) I		23
3-2		Cr 108 I		24
3-3		Cr 160 I		25
3-4		Cr 108.5 SmA (101.5) I		25
3-5		Cr 187 SmA (174) I		26

3-6		Cr 92 I	30.2[a]	27
3-7		Cr 28.5 N 42 I	11.1[b]	28,29
3-8		Cr 122 Sm 132 N 208 I		27
3-9		Cr 95.5 N 230 I		30

[a]Extrapolated from liquid-crystalline material at 25°C.
[b]$T_{meas} = 27°C$.

TABLE 4 Mesomorphic Properties of Some Liquid Crystals

No.	Compound	Phase transitions (°C)	Ref.
4-1		Cr 129 SmA 157.9 I	33
4-2		Cr 92.8 N 156.1 I	34
4-3		Cr 75.6 N 88 I	35

temperatures) in four-ring derivatives (compound **1-1**), whereas three-ring 2-oxetanone derivatives usually do not show the mesomorphic properties [4].

It has been demonstrated that 2-oxazolidinone is overall planar with C3-O2 bond length (1.219 Å) slightly longer than a C=O bond (1.201 Å) in lactones [9], although the C3-O1 bond (1.347 Å) is shorter than the corresponding C−O bond in γ-lactones (1.464 Å), revealing electronic delocalization from N to O1 via the C3-O2 group [9]. In this ring, the hydrogen bonds create a chained structure in the y direction, whereas molecules in parallel planes are connected by dipole–dipole and van der Waals interactions [9]. The coplanar approach of the NH group has been rationalized in terms of the ab initio calculated molecular electrostatic potential generated by the C=O group [9]. The data collated in Table 1 reveal that 5-methyl-2-oxazolidinone substitution in the four-ring derivative does not favor the formation of the mesophases (compound **1-2**), whereas the corresponding 4-methyl-2-oxazolidinone substitution results in the formation of high melting and narrow smectic C^* phase (compound **1-3**). This shows the importance of the molecular structure of liquid crystals containing 2-oxazolidinone. One more example of these liquid crystals is presented by compound **1-4**, where removing the bent methylene linkage, elongating the alkyl group, and even decreasing the number of the rings favors the smectic phase. The corresponding 2(3H)-dihydrofuranone derivatives are not mesomorphic (compounds **1-5**, **1-6**; see also compounds **1-9**, **1-10**, Table 1). These can be correlated with the geometric and electronic structure of 2(3H)-dihydrofuranone. It has been reported that this ring adopts mainly a twisted-ring conformation, which readily bends and twists in either direction from the

lowest-energy structure and undergoes rapid ring inversion via a planar (C_s) structure with a barrier of $4.7\,kJ \cdot mol^{-1}$ [10]. Envelope-like conformations with an out-of-plane angle of 29.7° for the flap may be present but perhaps do not represent a true equilibrium structure [10]. The envelope and twisted-ring (with a twist angle of 18.7°) conformations differ mainly in a vertical translation of C3 and C4 by ca. 0.14 Å with respect to the C2-C1-O2 plane [10]. This ring is substantially strained. Note that the corresponding tetrahydrofuran [11,12] derivatives show the smectic B and A phases with moderate thermostabilities (compounds **1-5**–**1-8**, Table 1). In this case, the carbonyl group in 2(3H)-dihydrofuranone derivatives works as lateral substituent broadening the molecule [13].

It has been reported that the tetrahydropyran ring is slightly flatter than cyclohexane [14]. Its molecule resembles cyclohexane in geometry excepting the short C-O bond (1.41 Å) compared to the C-C bond (1.54 Å). These two rings do have very similar chair-to-chair ring-reversal processes [14]. The corresponding tetrahydro-2H-pyran-2-one molecule has been found in the form of a flattened chair and in a boat form (more nearly a classical boat than a twisted boat) [15]. The chair form is rather unstable, caused by a strong tendency for the four-atom part of the carboalkoxy group to be planar. This leads to a dihedral angle of 36.9° about the C-O bond [15]. In the boat form of this molecule, the four atoms on the near side of the ring are nearly coplanar. The bow and stern hydrogens inside the ring are closer that they would like to be, and the molecule is twisted slightly to relieve this repulsion. These structural features and an eclipsed butane unit on the back side of the molecule reveal that both conformations are quite strained, with the boat more stable than the chair [15]. The strain is worse in the chair than in the boat, but it is less in 2(3H)-dihydrofuranone [15]. As expected, the observed structural features of tetrahydropyran and terahydro-2H-pyran-2-one should affect the mesomorphic properties of compounds incorporating them. As in the case of five-membered rings discussed previously, the exocyclic carbonyl group works again as lateral substituent, reducing the number of the mesophases and the clearing point (smectic–isotropic or nematic–isotropic or cholesteric–isoptropic phase-transition temperature) (compounds **2-1**, **2-2**, Table 2). As in the case of 2(3H)-dihydrofuranone derivatives, the *cis*-isomers of terahydro-2H-pyran-2-one derivatives are not mesomorphic, whereas their *trans*-isomers exhibit the chiral smectic C^* phase with moderate thermostabilities (compounds **2-1**, **2-3**, **2-4**, Table 2).

It has been shown that 1,3-dioxolan-2-one exists in the crystal form in a half-chair conformation with the torsional angle O-C4-C5-O

being 31° and a barrier to ring inversion of 2.7 $kJmol^{-1}$ [21,22]. The introduction of this ring into the molecular core of four-ring derivatives results in the formation of high-melting smectic A phase in the *trans*-isomer **2-5** and gives no mesophase for the *cis*-isomer **2-6** presented in Table 2. Similar trends can be observed for the 1,3-dioxolan-4-one derivatives (compounds **2-7**, **2-8**, Table 2), which exhibit significantly lower melting and clearing temperatures in comparison with those of the corresponding 2-oxetanone derivative **1-1** (for the *trans*-isomers).

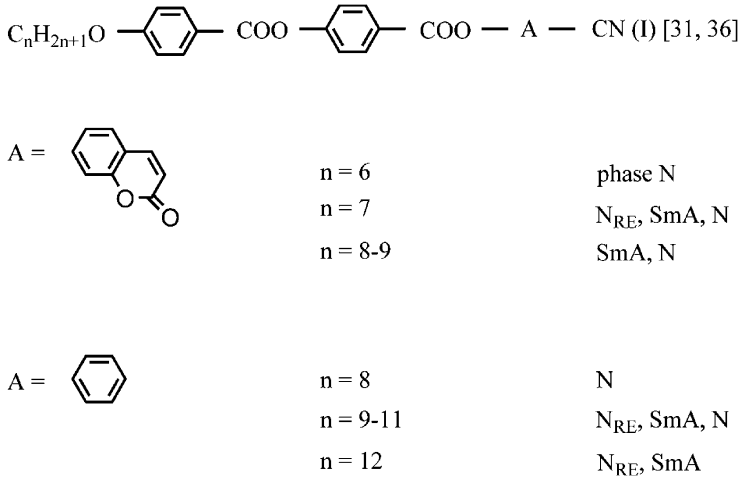
As is evident from Table 3, the introduction of 1,3-dioxan-2-one into the molecular core of two-ring derivatives creates the monotropic smectic A phase with significantly lower melting and clearing points in comparison with those of the corresponding reference ketones (compounds **3-1**, **3-3**–**3-5**, except the clearing point for compound **3-3**), whereas changing the substituents and their positions at 1,3-dioxan-2-one could lead to the disappearance of the mesomorphic properties (compound **3-2** where the dipole of the carbonyl group directs nearly perpendicular to the long molecular axis).

It can be seen from Table 3 that two-ring 2H-pyran-2-one cyano derivative shows no mesophase compared with the nematic cyano biphenyl (compounds **3-6**, **3-7**), whereas the introduction of 2H-pyran-2-one into the molecular core of three-ring cyano derivatives increases the melting temperature, introduces the smectic phase, and lowers the nematic thermostability in comparison with those of the corresponding 1,4-phenylene derivative (compounds **3-8**, **3-9**).

According to Takenaka *et al.* [31], the carbonyl group of 2H-1-benzopyran-2-one [32] forming an angle of 60° with respect to the long molecular axis enhances the lateral interactions due to the dipole–dipole interactions and can be responsible for the formation of only smectic A phase in two-fragment 2H-1-benzopyran-2-one cyano derivative **4-1** compared with the 1,4-phenylene- and 1,4-phenylene = based compounds **4-2**, **4-3** (Table 4). In the case of three-ring cyano derivatives presented in system (I), we say that the replacement of 1,4-phenylene by 2H-1-benzopyran-2-one creates the re-entrant nematic phase for only one, shorter homologue (Scheme 1).

Similar trends have been reported for other cyclic ester derivatives [36–74].

It can be proposed that the electronic and geometric structures of ester-containing rings [2,3,9,10,15,21,22,32] play a very important role in the intra- and intermolecular interactions [75–77] that affect the packing of the molecules and that predominantly influence mesophase stability [29,75–78]. Anisotropic dispersion interactions, and consequently the anisotropy of polarizability, depending on the electron



SCHEME 1 Mesomorphic properties of some liquid crystals.

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 [78]. Other molecular aspects such as the association [29] or dipole–dipole attraction in polar liquid-crystalline derivatives, which can influence the packing of the molecules, also affect the stability of the mesophases [78].

3. STATIC DIELECTRIC PROPERTIES

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are dielectric constants that are parallel and perpendicular, respectively, to the nematic director **n**, and molecular structure of liquid crystals is described by the theory of Maier and Meier [79]:

$$\Delta\varepsilon = \frac{\mathrm{NhF}}{\varepsilon_o}\left[\frac{\Delta\alpha - \mathrm{F}\mu^2}{\mathrm{kT}(1 - 3\cos^2\beta)}\right]\mathrm{S}, \tag{1}$$

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, 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.

As is evident from Table 3, the replacement of 1,4-phenylene ($\mu = 0$ [80]) by 2H-pyran-2-one increases the dielectric anisotropy because

the total dipole moment is increased (compounds **3-6**, **3-7**). It is rough comparison because the dipole moment is only available for the corresponding 4H-pyran-4-one, $\mu = 3.72$ D [81].

4. PHYSICAL PROPERTIES OF THE SMECTIC C* PHASE

The spontaneous polarization P_s of the smectic C* liquid crystals is an important parameter because of its linear coupling with an applied electrical field, which is the basis of the application of these materials [82]. The polarization is caused by the cramped rotation of the dipoles of the molecules and varies with the position of these dipoles with respect to the chiral group [82]. The spontaneous polarization P_s is a quantity that is directly related to the response time τ as a switching device [83]:

$$\tau = \frac{\gamma_\phi \sin^2 \Theta}{P_s E}, \tag{2}$$

where γ_ϕ is the rotational viscosity, which refers to the rotation about an axis perpendicular to the director **n** and P_s, Θ is the tilt angle, and E is an applied electric field.

It has been demonstrated that the spontaneous polarization of the ferroelectric liquid crystals are related to the sum of the vectors of the dipoles in the tilted smectic phases [84,85], and the magnitude of the P_s of chiral liquid crystals depends on the magnitude of the dipole near the chiral center and on the restriction of the rotational freedom around the chiral center [85].

As is evident from Tables 1 and 2, the introduction of the chiral, ester-containing rings into the molecular structure of liquid crystals in many cases gives the high values of spontaneous polarization, whereas larger values of P_s and Θ and lower values of the response times recorded for the *cis*-isomers in comparison with those of the corresponding *trans*-isomers (compounds **1-5**–**1-10, 2-3**–**2-8**) have been explained in terms of molecular packing, which is more ordered and provides a nearly perpendicular direction of the dipole moment of these rings to the longitudinal molecular axis [6,8,16,18,44,46,48,66]. As expected, *trans*-2-oxetanone derivative **1-1** (which has a smaller chiral ring) exhibits a lower response time than the corresponding *trans*-1,3-dioxolan-4-one derivative **2-7**, although the latter compound shows a significantly higher spontaneous polarization, which is due to its increased dipole moment (compare roughly $\mu = 4.17$ D [86] of 2-oxetanone and $\mu = 5.35$ D [22] of 1,3-dioxolan-2-one). In the case of the 2-oxazolidinone derivatives **1-2**–**1-4**, their unknown enantiomeric purity makes it difficult to compare them

with the 3H-dihydrofuran-2-one derivatives in terms of the ferroelectric parameters. The data presented in Table 1 and Ref. [47] reveal that the replacement of the 3H-dihydrofuran-2-one ($\mu = 4.0$ D [15]) by less viscous tetrahydrofuran (with a smaller dipole moment $\mu = 1.8$ D [87]) consequently lowers the spontaneous polarization and response times (compare g and f measurements) (compounds **1-6**, **1-8**).

5. CONCLUSION

Systematic studies of the introduction of cyclic esters into the molecular structure of liquid crystals on the creation of the mesophases and their physicochemical and electro-optical 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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