



Introducing the azocinnamic acid scaffold into bent-core liquid crystal design: A structure–property relationship study



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ABSTRACT

A series of bent-core liquid crystals possessing the azocinnamoyl unit in both elongating side arms was synthesized. The chain length was kept fixed for each molecule (C₁₂H₂₅), whereas the substituents at the central and outer rings were varied. The LC phases were assigned by polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. The investigated compounds are suitably diverse to reveal some aspects of the relationship between molecular structure and the mesomorphic properties. Namely, non-substituted parent compound is crystalline only and the methyl group in position 2 or the chlorine atom in position 4 of the central ring suppresses LC phase formation. Introduction of the strong electron-withdrawing nitro group between the side arms on the central ring leads to a B₇ phase. Compounds possessing a bromine atom or two chlorine atoms in the neighbourhood of the ester groups form LC phases typical for rod-like molecules, namely a nematic – smectic phase sequence. The results are compared with those reported for the azobenzoyl analogues.

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1. Introduction

For development of new liquid crystalline (LC) materials with potential for innovative applications, it is essential to select appropriate building blocks and to arrange them in suitable structural geometries. In this way, complex systems can be produced with control over the assembly processes and material properties. Namely, building blocks can be functionalized to enable responsiveness, electron-conductivity or certain biologically relevant functions. Thus, research of possibilities to modulate LC properties through synthetic design of building blocks is still progressing [1–3].

The first investigation of relatively simple cinnamoyl-based LCs, methyl and ethyl 4-(4-alkoxyphenylazo)cinnamates, was reported by Vorländer in 1937 [4] and since then this unit has been applied to LC materials as thermotropic [5–7] and polymeric systems [8–10]. In comparison to benzoyl analogues, the ethylene group between the phenyl ring and the carboxylate group in those

derived from cinnamic acid enhances the longitudinal polarisability and extends the molecular length.

Regarding thermotropic systems, the bent-core LCs incorporating the cinnamoyl unit are less considered than rod-like ones. The lack of investigation probably masks the inherent interest in these compounds as evidenced by studies describing full characterization of LC features of both symmetric and non-symmetric bent-core LCs with the cinnamoyl unit. A variety of LC phases (B₁, B₃ and B₆) has been reported in the homologous series derived from molecules based on unsubstituted or methyl-substituted resorcinol bis(cinnamoylalkoxybenzoates) [11]. Introduction of 4-chlororesorcinol as the central ring has led to compounds which exhibit a nematic phase at low temperatures and a SmC phase appearing as a monotropic phase [12]. 2-Methylresorcinol and 5-chlororesorcinol have been esterified with 4-(4-*n*-hexadecyloxy phenoxycarbonyl)cinnamic acid to give the compounds, which exhibit two enantiotropic LC phases [13]. The high-temperature phase of the former compound can be defined as a Col_F and the low-temperature phase is a racemic SmC_sP_A phase. In the case of latter, on cooling from the isotropic liquid textures typical for SmCP phases can be observed, while the low-temperature phase

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was assigned as a SmX. Out of symmetric bent-core LCs with a cinnamoyl unit in the outer position of the side arms, those based on 2,7-dihydroxynaphthalene are especially interesting as certain homologues exhibit a direct transition from an antiferroelectric B₂ phase to a nematic phase [14,15]. Bent-core LCs wherein the terminal alkynyl chains are connected with the terminal rings of the aromatic core by means of cinnamic esters form different polar phases (SmCP, Col, B₇) [16].

Kohout and coworkers provided several examples of non-symmetric bent-core LCs incorporating a cinnamoyl unit. Depending on the orientation of the ester group in one of the side arms, bent-core LCs based on 3-hydroxycinnamic acid formed either B₁ or B_{1Rev} phases, while one compound exhibited the B₂–B₅ phase sequence [17]. Non-symmetric bent-core LCs based on 4-chlororesorcinol with the azobenzene unit in one side arm and the cinnamoyl unit in another exhibited only a nematic phase [18].

A few heterocyclic ring systems have also been incorporated as a central core in bent-core mesogens. Isoxazole derivatives bearing a cinnamoyl unit in a side arm showed a tilted SmC mesophase and an orthogonal SmA mesophase in a wide temperature range, while the tetrazole analogues exhibited only a nematic mesophase [19]. LC compound with the 2,5-diphenylthiophene central core has been shown to form a SmA phase [20].

Effects of photoisomerization of the double bond proceeding *via* different mechanisms on the supramolecular arrangement have been widely investigated [21,22]. When illuminated by UV light of wavelengths longer than 300 nm, the cinnamoyl unit can undergo several photochemical processes. These involve not only E-Z isomerisation, but also cyclisation and the photo-Fries rearrangement [23,24]. Thus, applying these changes to induce transition between mesophases or to change mesophase parameters can pave a way for new photoresponsive systems. Recently, a photochemical study of a rod-like cinnamoyl-based reactive mesogen in solution showed that only E-Z isomerisation was operative under illumination with UV light (366 nm) for 30 min, [2 + 2] cycloaddition did not occur in solution [25]. It is suggested that cycloaddition requires close proximity of the molecules and the molecules in the solution are rather isolated.

Herein, we report the synthesis and physical study of a series of bent-core LCs possessing the azocinnamoyl units in the elongating side arm (Fig. 1). Actually, the motivation underpinning this study is to combine different photoresponsive groups into one molecule. The chain length was kept fixed for each molecule (C₁₂H₂₅–), whereas the substituents at the central and outer rings were varied based on their electronic and steric effects. As a result of a higher rigidity and a larger charge delocalisation, different mesomorphic

behaviour of the studied mesogens can be expected in comparison to analogues bearing the azobenzoyl unit.

Shruthi et al. have reported an optical storage device fabricated using structurally-related bent-core LC with the azobenzoyl unit in one side arm and the cinnamoyl in another, that exhibited stable bright and dark regions between crossed polarizers upon light illumination with a wavelength of 365 nm through a mask [26]. This observation can trace a path towards future applications of the compounds presented within this study.

2. Results and discussion

2.1. Synthesis

The five-ring structure of the mesogenic core was constructed as presented in Scheme 1. Firstly, the nitro group of compound **1** was reduced to give the compound **2** using zinc and hydrochloric acid as described elsewhere [27]. Following the procedure of Vorländer [4], the amino group of **2** was subsequently diazotized and the diazonium salt was coupled with phenol or 2-fluorophenol to afford methyl 4-(4-hydroxyphenylazo)cinnamate (**3a**) or methyl 4-(3-fluoro-4-hydroxyphenylazo)cinnamate (**3b**), respectively. The acids **5a** and **5b** were prepared by conventional alkylation of these compounds, followed by deprotection to the free carboxylic acid under basic conditions. In the final step, resorcinol or substituted resorcinol was acylated with chlorides of acid **5a** or **5b** in the presence of triethylamine affording the investigated compounds. A detailed description of the synthesis of representative intermediates and the investigated compounds and their structural characterization are presented in Supplemental file (Figs S1–S7).

2.2. LC behaviour

Combining the POM, DSC and XRD observations, the phase sequences of compounds **1a–g** were revealed, and the determined phase transition temperatures and associated enthalpy changes are summarized in Table 1.

Compounds **1a**, **1b** and **1d** show no mesogenic properties, they melt directly to isotropic liquid and recrystallize with a small hysteresis, preventing observation of potential monotropic LC phases. Compound **1c** with the NO₂ group in position 2 of the central ring also melts directly to isotropic liquid, however on cooling a liquid crystalline behaviour appears. Based on the characteristic optical texture with spiralling features, circular domains and fragmented fans (Fig. 2) the phase can be identified as B₇ [28], one of the phases

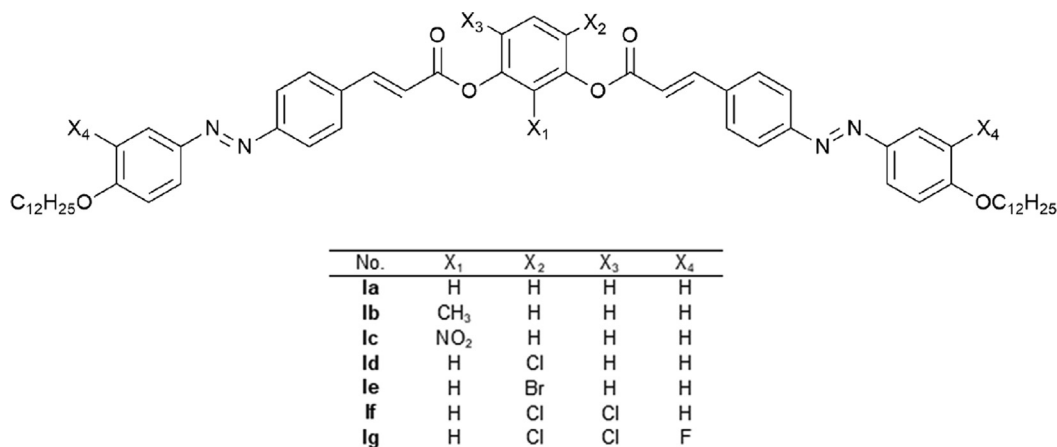
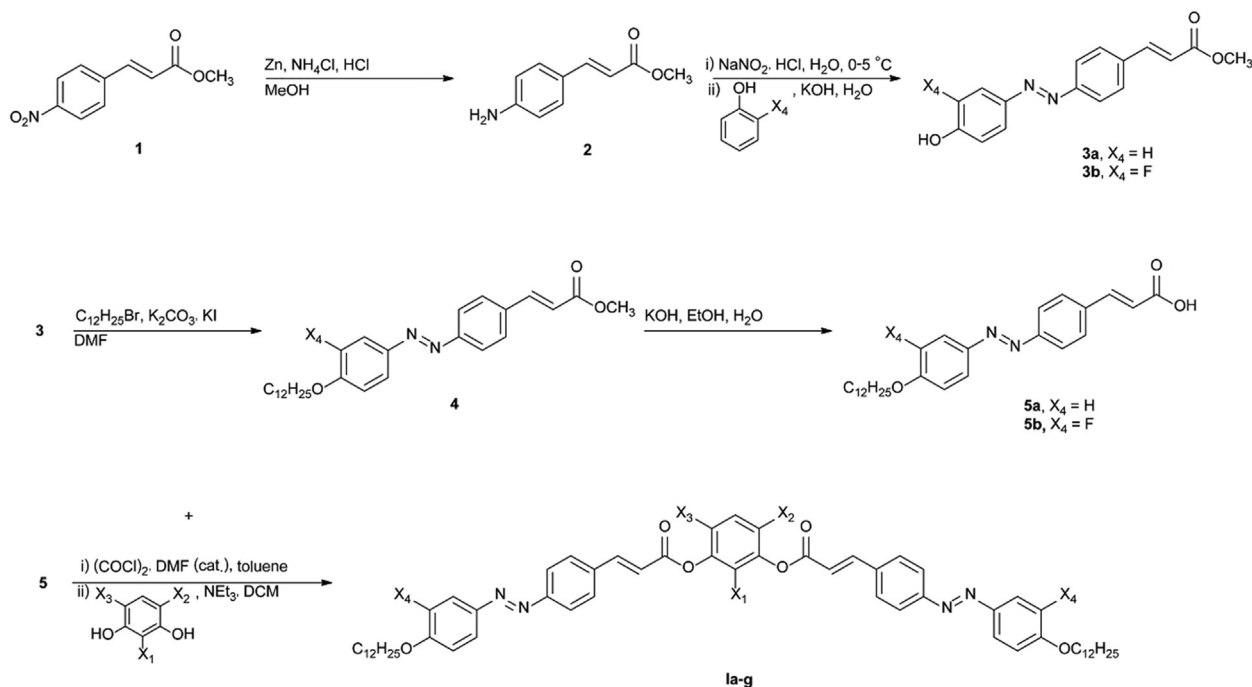


Fig. 1. Chemical structures of the investigated compounds.

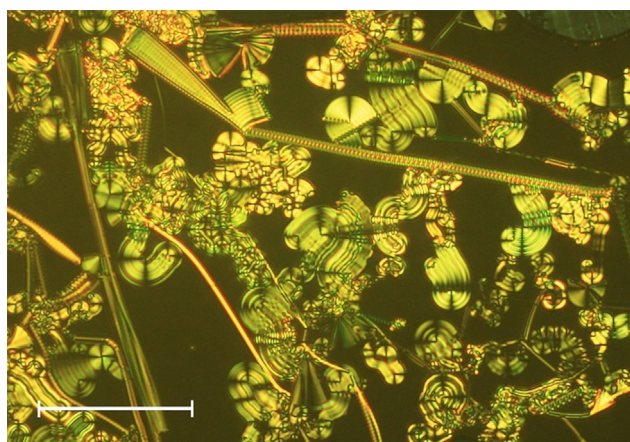


Scheme 1. Synthesis of the investigated compounds.

Table 1

The phase transition temperatures (in parentheses enthalpy changes) and the LC phase types of the investigated compounds.

No	X ₁	X ₂	X ₃	X ₄	m.p., T / °C (ΔH / J g ⁻¹)	Phase sequence on cooling, T / °C (ΔH / J g ⁻¹)
1a	H	H	H	H	159.0 (14.7)	Iso 151.0 (25.8) Cr
1b	CH ₃	H	H	H	176.5 (26.6)	Iso 168.6 (35.5) Cr
1c	NO ₂	H	H	H	163.5 (30.3)	Iso 160.4 (18.0) B ₇ 116.2 (10.0) Cr
1d	H	Cl	H	H	142.4 (39.1)	Iso 134.4 (42.5) Cr
1e	H	Br	H	H	142.2 (56.5)	Iso 146.8 (1.0) N 131.3 (9.8) SmC 112.3 (30.7) Cr
1f	H	Cl	Cl	H	135.5 (48.8)	Iso 180.20 (3.6) N 129.3 (1.1) SmC 92.0 (47.4) Cr
1g	H	Cl	Cl	F	97.4 (20.5)	Iso 169.6 (5.3) SmC 62.4 (24.3) Cr

Fig. 2. Optical texture observed for compound 1c between crossed polarizers at the Iso-B₇ phase transition. Scale bar represents 50 μm.

characteristic for bent-core mesogens. This might be expected as several examples from the literature show that the strong electron-withdrawing NO₂ group in the obtuse angle of the bent-core molecules leads to a B₇ phase. Actually, this phase has been reported for LCs possessing only the ester linking groups between

the aromatic rings [29] and those where the aromatic rings are connected by the ester and azomethine groups [30].

The phase identification is confirmed by X-ray diffraction (XRD) studies. In B₇ phase, a rich diffraction pattern was recorded (Fig. 3), with numerous sharp peaks at low angle range and diffused scattering at high-angle range. As the low-angle signals are incommensurate, they cannot result from a simple lamellar structure, however, their positions can be well fitted assuming 2D electron density modulations with oblique crystallographic unit cell, with parameters $a = 116.9 \text{ \AA}$, $b = 43.5 \text{ \AA}$ and $\gamma = 113.5^\circ$ (Fig. 3b). Accordingly, structure of B₇ phase can be pictured as periodically undulated (or broken) layers - blocks, organized into two-dimensional lattice. It should be noted that neighbouring molecules inside the layer fragments show only short-range positional correlations.

Compounds 1e-g show enantiotropic mesomorphic properties and they all form LC phases typical for rod-like molecules: 1e and 1f exhibit a nematic – smectic phase sequence, while for 1g a nematic phase is destabilized and a smectic phase is formed directly from isotropic liquid. It should be noted that in 1e and 1f compounds smectic phase is monotropic, and could be observed only in supercooled samples. Based on optical microscopy studies the smectic phase in all compounds 1e-g was identified as tilted smectic C phase. Characteristic fingerprint texture was observed for one-free-surface samples at the transition from a nematic phase (Fig. 4a). Additionally, in cells with planar anchoring condition and unidirectional rubbing tilted domains were formed, that

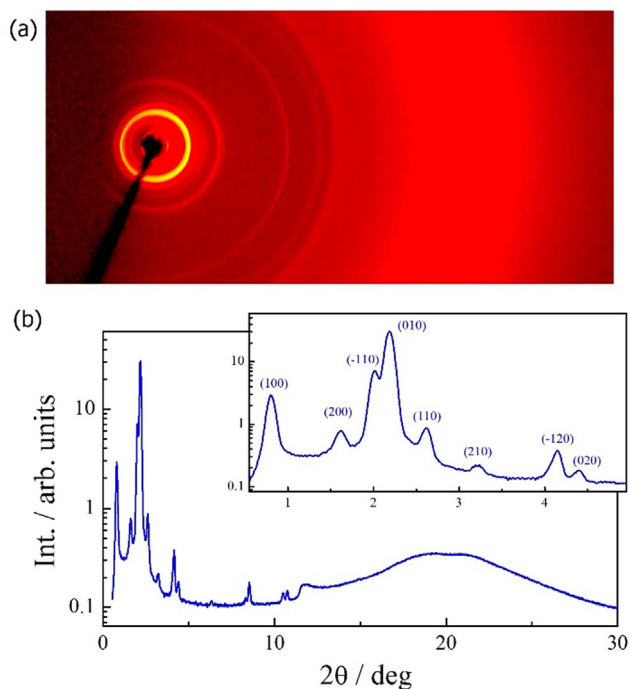


Fig. 3. (a) 2D XRD pattern recorded in the B₇ phase of compound **Ic** at T = 150 °C. (b) Diffracted intensity vs. diffraction angle obtained by integration of the pattern given in (a) over azimuthal angle. Diffused high angle signal points to liquid crystalline character of the phase. In the inset, enlarged small angle range with the (hkl) indices of the signals.

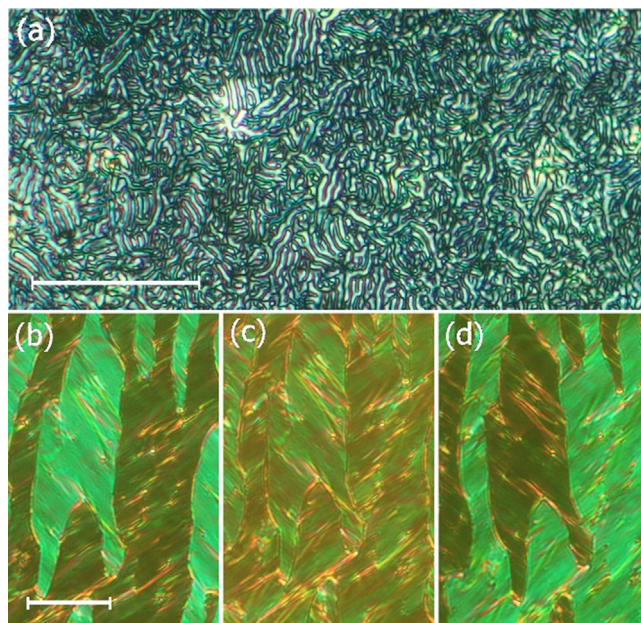


Fig. 4. Optical textures observed for (a) compound **Ic** in one-free-surface sample at the N–SmC phase transition and (b–d) compound **If** in SmC phase in cell with planar anchoring, in (b) and (d) the sample was rotated by $\pm 7^\circ$ with respect to (c). Scale bars represent 100 μm .

could be brought into extinction condition by rotating the sample with respect to crossed polarizers (Fig. 4b–d).

The phase identification was confirmed by X-ray diffraction. In the wide angle diffraction pattern there were a series of narrow, commensurate low angle signals, evidencing well-defined layered structure, while the broad high angle signal points to liquid-like

order of molecules within the layers (Fig. S8, Supplemental file). The layer spacing, d , in SmC phase decreases on cooling (Fig. 5), due to molecular tilt with respect to layer normal. For compound **Ic** it was not possible to obtain $d(T)$ dependence because of rapid recrystallization, and the value of $d = 40 \text{ \AA}$ was found at 130 °C. Interestingly, the layer thickness was much different for compounds **Ie–Ig**, despite the similar molecular structure. Most probably attachment of different substituents at central ring has pronounced effect on molecular conformation (opening angle of bent molecule). Different molecular conformations might be also responsible for the difference in the optical birefringence of the nematic phase formed by **Ie** and **If** compounds (Fig. S9, Supplemental file), with Δn values measured for the latter being $\sim 20\%$ higher.

It should be noted, that although being composed of bent-core molecules the SmC phase of compounds **Ie–Ig** did not show polar properties, neither optical switching, nor repolarization current was observed under application of ac electric field. Also, measurements of dielectric constant pointed to apolar character of the phase.

2.3. Comparison with the bent-core benzoyl analogues

The phase transition temperatures and the LC phase types of the bent-core benzoyl analogues with the same or longer alkyl chains having the same substituent in the central ring, reported in literature, are listed in Table 2.

It has been shown that 1,3-phenylene bis-(4-(4-dodecyloxyphenylazo)benzoate) (**IIa**) and higher homologues of those with the CH₃ (**IIb**) or NO₂ group (**IIc**) in position 2 of the central ring exhibit no LC phase [31]. Contrary to compound **Ic**, introduction of the strong electron-withdrawing NO₂ group between the arms in the central ring of the benzoyl analogue suppresses the LC phase formation.

Comparing to compounds possessing halogen substituents on the central ring presented here, the LC behaviour of the benzoyl analogues also differs. In compounds **IIc** and **IIe**, which have the Cl or Br atom in position 4 of the central ring, a monotropic nematic phase was observed [32]. Substitution of the H atom in position 6 of the central ring in **IIc** by an additional Cl atom led to a compound **IIc'** that also exhibited the monotropic nematic phase, but with somewhat higher clearing temperature [33]. The nematic phases in these three compounds are expected to be cybotactic nematic phases as typical for bent-core LCs [32,33].

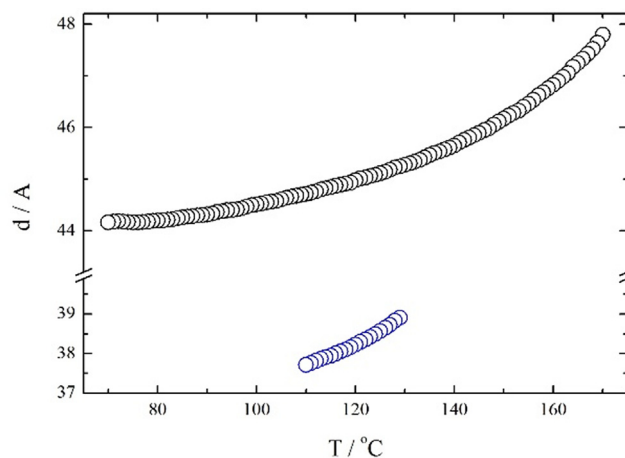
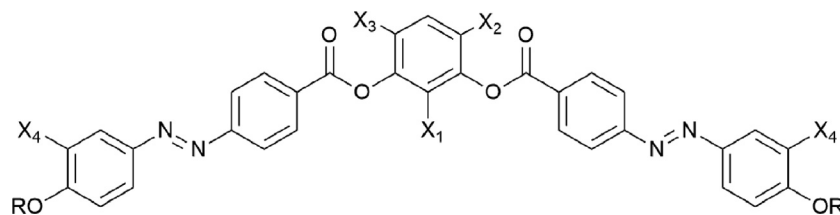


Fig. 5. Temperature dependence of layer spacing in the SmC phase of compounds **If** (blue) and **Ig** (black).

Table 2

The phase transition temperatures and the LC phase types of the bent-core benzoyl analogues.



No.	X ₁	X ₂	X ₃	X ₄	R	Phase sequence, T [°C]	Ref
Ila	H	H	H	H	C ₁₂ H ₂₅	Iso 136.2 Cr	[31]
Ilb	CH ₃	H	H	H	C ₁₆ H ₃₃	– ^a	[31]
Ilc	NO ₂	H	H	H	C ₁₆ H ₃₃	– ^a	[31]
Ild	H	Cl	H	H	C ₁₂ H ₂₅	Iso 94 N 78 Cr	[32]
Ile	H	Br	H	H	C ₁₂ H ₂₅	Iso 89 N 83 Cr	[32]
Ilf	H	Cl	Cl	H	C ₁₂ H ₂₅	Iso 122 N 107 Cr	[33]
Ilg	H	Cl	Cl	F	C ₁₆ H ₂₃	Iso 105 Cr	[33]

^a compounds were reported to be non-mesogenic, but the melting points were not given.

The conformation of the half-parts of the bent-core molecules is predominantly determined by the geometry of the ester linking group between the central ring and the side arms [34]. While describing the LC features of the 4,6-dichloro-1,3-phenylene bis (4-(4-*n*-alkoxy-phenyliminomethyl)benzoates, Weissflog and coworkers have indicated that, when the number of substituents on the central ring in *ortho* position to the ester linking groups increases, the strong deformation of the ester groups on this ring makes the molecule more linear [35]. Molecular simulations have indicated that the electrostatic repulsion between the halogen substituents and the oxygen atoms in the ester linking groups leads to a torque exercised on the side arms [36]. The core becomes twisted and the angle between the *para* axes of the rings in the side arms and the long molecular axis decreases. Thus, it can be expected that the ethylene group between the phenyl ring and the ester linking group of the cinnamoyl unit changes the molecular shape additionally, so the resulting LCs most likely have a nearly stretched conformation. In this way, formation of LC phases typical for rod-like LCs can be explained. In comparison to the benzoyl analogues, this stretched conformation leads to the higher clearing temperatures and a wider LC phase ranges.

Considering effects of the substituents in the outer ring, further introduction of the F atom in the molecular structure of **Ig** reduces the clearing point and destabilizes the nematic phase, while in the case of the benzoyl analogue **Ilg**, the complete loss of LC behavior takes place.

2.4. UV illumination-induced changes in LC order

Illumination of samples with UV light (365 nm) will change the conformation of the azo group in the side arms of the investigated molecules. The magnitude of associated changes in the LC packing order then dictates how these changes affect the mesophase. The largest change was observed in the SmC phase of compounds **Ie** and **If**. An example is shown in Fig. 6. The characteristic patchy structure of the SmC phase in planar cells was realigned upon illumination, so that the direction of the optical axis became uniform all over the observation area. However, the domain walls remained visible. These changes were fast (switching on time 160 ms, switching off time 380 ms) and reversible, which is indicative of optical switching. This phenomenon was only observed in samples that possess two successive phases (nematic and smectic).

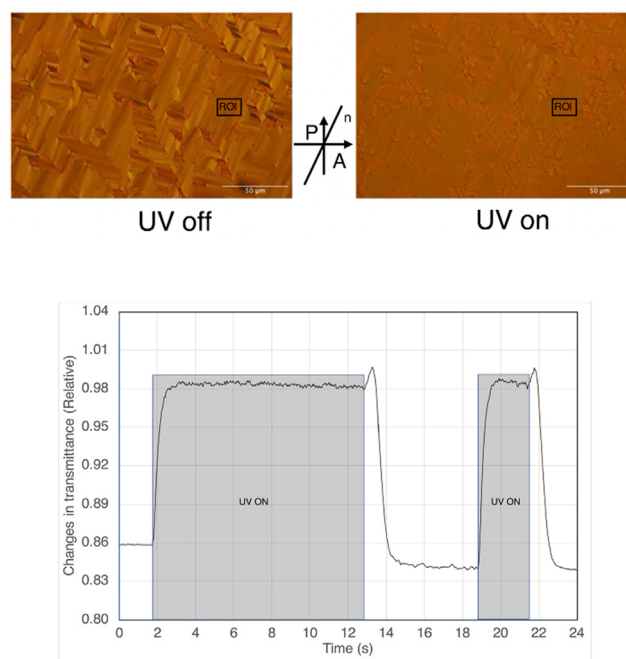


Fig. 6. UV illumination-induced changes of the texture revealed by the POM imaging. Up: POM image observed without and with the UV illumination. Bottom: Changes in optical transmittance over time.

3. Conclusion

To meet demands of emerging technologies, especially optical data storage, the design and preparation of new LCs is highly desirable. In this work, we report the synthesis and study of a series of bent-core LCs possessing the azocinnamoyl unit in the side arms. The mesomorphic properties have been tuned by introducing a variety of substituents in the central and outer rings. In some aspects, the observed relationship between the molecular structure and the mesomorphic properties of the investigated compounds agrees with the results reported for the series of bent-core LCs possessing only the ester linking groups between the phenyl rings. Non-substituted parent compound and those bearing the CH₃ group in position 2 or the Cl atom in position 4 of the central ring are non-mesogenic. Interestingly, introduction of the NO₂

group reveals a different type of LC phase to those observed in less polar LC compounds within the series, namely a B₇ phase. The other compounds form enantiotropic LC phases typical for rod-like molecules. Compound bearing the Br atom in position 4 or the Cl atoms in positions 4 and 6 of the central ring exhibit a nematic – smectic phase sequence. On the other hand, introduction of the F atoms in the outer rings destabilizes the nematic phase, but the LC character of the compound remains. When comparing to azobenzoyl analogues, the stretched molecular conformation of these LCs has led to the higher clearing temperatures and wider LC phase ranges. Interestingly, the optical switching was only observed in samples that possess two successive LC phases. Changes in birefringence were large, fast and reversible, which indicates the optical response.

We consider that the results presented here will serve researchers to establish guidelines for new LCs possessing the azocinnamoyl unit. Interesting selectivity of the optical switching requires additional research on the underlying mechanisms.

4. Experimental

4.1. Materials and methods

All the chemicals and solvents were obtained from commercial sources and used without any further purification. The synthetic steps of the investigated compounds are given in [Scheme 1](#). As previously stated, compounds **2** and **3** were prepared according to procedures from the literature [4,27]. The complete synthetic procedures and analytical data are reported in the ESI.

4.2. Characterization of the mesomorphic properties

Phase transition temperatures and associated enthalpy changes were determined by differential scanning calorimetry (DSC) performed with a TA DSC Q200 calorimeter. Both, heating and cooling scans were performed with a rate of 10 K/min. Samples of mass from 1 to 3 mg were measured, sealed in aluminum pans and kept in nitrogen atmosphere during the measurement.

Observations of characteristic optical textures of the LC phases were conducted using a Zeiss Axio Imager A2m polarized light microscope equipped with a Linkam heating stage. The samples were placed either between two untreated thin glass slides or in glass cells with planar anchoring induced by a thin inner layer of polymer. The cells were filled by capillary action with the material in the isotropic liquid phase. One-free-surface samples were also used to induce homeotropic alignment.

Optical birefringence was measured using a setup including: a photoelastic modulator (PEM-90, Hinds) working at a modulation frequency 50 kHz, a halogen lamp (Hamamatsu LC8) equipped with a narrow band pass filter (532 nm) and a photodiode (FLC Electronics PIN-20). Time-dependent transmitted light intensity was deconvoluted with a lock-in amplifier (EG&G 7265) to yield a retardation induced by the sample.

The wide angle X-ray diffraction patterns were obtained with the Bruker D8 GADDS system (CuK α incident beam formed by Goebel mirror and point beam collimator, Vantec 2000 area detector, modified Linkam heating stage). Temperature dependence of smectic layer thickness was determined from small angle XRD studies performed with Bruker D8 Discover system (CuK α incident beam formed by Goebel mirror, scintillation counter, Anton Paar DCS350 heating stage). Samples for diffraction experiments were prepared as droplets / thin films on a heated surface.

Recorded diffraction patterns were analyzed using Topas 3 software package, which allowed for precise determination of individual diffraction signal positions and thus related structure

periodicity (e.g. layer thickness in SmC phase), as well as for fitting the geometrical parameters of multi-dimensional crystallographic lattice based on the whole diffraction pattern.

UV switching experiments were done on samples in planar LC cells (Instec 8 μ m thick, antiparallel planar rubbing). Experimental setup was home-built from a commercial heating stage (Instec MK1) which was retrofitted with UV illumination lamp (365 nm LedEngin LED) providing homogeneous illumination on the whole sample. Optical power was measured to be 40mW (Coherent Lab-Max TOP with PM1) on the surface of the LC cell. Observations and measurements were done through a POM microscope (Nikon Optiphot II) with video capabilities.

CRedit authorship contribution statement

Kristina Gak Simić: Investigation, Formal analysis, Validation, Writing – original draft. **Paulina Rybak:** Investigation, Formal analysis, Validation. **Damian Pocięcha:** Investigation, Writing – review & editing. **Luka Cmok:** Investigation, Writing – review & editing. **Irena Drevenšek-Olenik:** Investigation, Writing – review & editing. **Tibor Tóth-Katona:** Investigation. **Nemanja Trišović:** Conceptualization, Supervision, Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2022.120182>.

References

- [1] Y. Wang, Q. Li, Light-driven chiral molecular switches or motors in liquid crystals, *Adv. Mater.* 24 (2012) 1926–1945, <https://doi.org/10.1002/adma.201200241>.
- [2] Z. Hassan, Y. Matt, S. Begum, M. Tsotsalas, S. Bräse, Assembly of molecular building blocks into integrated complex functional molecular systems: Structuring matter made to order, *Adv. Funct. Mater.* 30 (2020) 1907625, <https://doi.org/10.1002/adfm.201907625>.
- [3] K. Long, Y. Liu, Y. Li, W. Wang, Self-assembly of trigonal building blocks into nanostructures: molecular design and biomedical applications, *J. Mater. Chem. B* 8 (2020) 6739–6752, <https://doi.org/10.1039/D0TB01128B>.
- [4] D. Vorländer, R. Wilke, U. Haberland, K. Ost, Krystallin flüssige Kombinationen von p-Azozimtsäure-estern mit p-Azo-phenol-Derivaten; ein Beitrag zur Kenntnis der Assoziations-Vorgänge, *Her. Dtsch. Chem. Ges.* 70 (1937) 2096–2108.
- [5] N. Kasthuraiah, B.K. Sadashiva, S. Krishnaprasad, G.G. Nair, Synthesis and mesomorphic properties of some esters of trans-4-n-alkoxycinnamic and trans-4-n-alkoxy-alpha-methylcinnamic acids exhibiting ferroelectric and antiferroelectric phases, *Liq. Cryst.* 24 (1998) 639–645, <https://doi.org/10.1080/026782998206740>.
- [6] B.T. Thaker, J.B. Kanojiya, Mesomorphic properties of liquid crystalline compounds with biphenyl moiety containing azo-ester, azo-cinnamate central linkages and different terminal group, *Liq. Cryst.* 38 (2011) 1035–1055, <https://doi.org/10.1080/02678292.2011.594525>.
- [7] R.R. Koshti, A. Vyas, H.N. Patel, A.K. Prajapati, Mesogenic homologous series with a butoxyethyl terminal chain, *Liq. Cryst.* 48 (2021) 1859–1872, <https://doi.org/10.1080/02678292.2021.1902580>.
- [8] K. Ichimura, Y. Akita, H. Akiyama, K. Kudo, Y. Hayashi, Photoreactivity of polymers with regioisomeric cinnamate side chains and their ability to

- regulate liquid crystal alignment, *Macromol.* 30 (1997) 903–911, <https://doi.org/10.1021/ma961225q>.
- [9] M. Kondo, Y. Dozono, K. Goto, N. Kawatsuki, Synthesis of side-chain liquid-crystalline cinnamide polymers based on post polymer reaction, *Mol. Cryst. Liq. Cryst.* 563 (2012) 121–130, <https://doi.org/10.1080/15421406.2012.689142>.
- [10] P. Wei, W. Zhang, Y. Zhang, Y. Wang, Z. Guo, H. Yu, Y. Xia, Y. Wang, Y. Wang, Direct synthesis of potentially biodegradable aromatic–aliphatic thermotropic copolyesters with photocrosslinking properties, *Liq. Cryst.* 46 (2019) 1780–1789, <https://doi.org/10.1080/02678292.2019.1600751>.
- [11] E. Mátyus, K. Fodor-Csorba, Synthesis and liquid crystal properties of new banana-shaped cinnamoyl derivatives, *Liq. Cryst.* 30 (2003) 445–450, <https://doi.org/10.1080/0267829031000089906>.
- [12] E. Mátyus, K. Keserű, Synthesis, characterization and theoretical considerations of a novel class of banana-shaped compounds with liquid crystal properties, *J. Mol. Struct. THEOCHEM* 543 (2001) 89–98, [https://doi.org/10.1016/S0166-1280\(00\)00845-9](https://doi.org/10.1016/S0166-1280(00)00845-9).
- [13] W. Weissflog, G. Pelzl, H. Kresse, U. Baumeister, K. Brand, M.W. Schröder, M.G. Tamba, S. Findeisen-Tandel, U. Kornek, S. Stern, A. Eremin, R. Stannarius, J. Svoboda, In search of a new design strategy for solid single-component organic ferroelectrics: Polar crystalline phases formed by bent-core molecules, *J. Mater. Chem.* 20 (2010) 6057–6079, <https://doi.org/10.1039/C0JM00322K>.
- [14] R. Amaránatha Reddy, B.K. Sadashiva, S. Dhara, Banana-shaped mesogens: observation of a direct transition from the antiferroelectric B₂ to nematic phase, *Chem. Commun.* (2001) 1972–1973, <https://doi.org/10.1039/B106458B>.
- [15] R. Amaránatha Reddy, B.K. Sadashiva, V.A. Raghunathan, Banana-shaped mesogens derived from 2,7-dihydroxynaphthalene and 1,3-dihydroxybenzene: Novel columnar mesophases, *Chem. Mater.* 16 (2004) 4050–4062, <https://doi.org/10.1021/cm0494498>.
- [16] G. Pelzl, M.G. Tamba, S. Findeisen-Tandel, M.W. Schröder, U. Baumeister, S. Diele, W. Weissflog, New bent-core mesogens with carbon–carbon multiple linkages in the terminal chains, *J. Mater. Chem.* 18 (2008) 3017–3031, <https://doi.org/10.1039/B803493A>.
- [17] M. Kohout, J. Tůma, J. Svoboda, V. Novotná, E. Gorecka, D. Pocięcha, 3-Hydroxycinnamic acid – a new central core for the design of bent-shaped liquid crystals, *J. Mater. Chem. C* 1 (2013) 4962–4969, <https://doi.org/10.1039/C3TC30664j>.
- [18] M. Šmahel, A. Poryvai, Y. Xiang, D. Pocięcha, T. Troha, V. Novotná, J. Svoboda, M. Kohout, Photosensitive bent-core nematic liquid crystals with various linking units in the side arms: Structure–properties relationships, *J. Mol. Liq.* 306 (2020) 112743, <https://doi.org/10.1016/j.molliq.2020.112743>.
- [19] R.R. da Rosa, M. Tariq, C.S.B. Weber, S. Hameed, S. Silva, A.A. Merlo, Hybrid liquid crystals tetrazolyl and isoxazolyl cinnamates, *Liq. Cryst.* 43 (2016) 1659–1670, <https://doi.org/10.1080/02678292.2016.1193908>.
- [20] W. Zhang, W.L. He, C. Di, X. Wang, Z. Yang, D. Wang, H. Cao, D. Yang, H. Yang, Effects of thiophene-based mesogen terminated with branched alkoxy group on the temperature range and electro-optical performances of liquid crystalline blue phases, *Liq. Cryst.* 43 (2016) 524–534, <https://doi.org/10.1080/02678292.2015.1124465>.
- [21] R.S.H. Liu, L.-Y. Yang, Y.-P. Zhao, A. Kawanabe, H. Kandori, in: *Supramolecular Photochemistry: Controlling Photochemical Processes*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2011, pp. 547–570.
- [22] D.E. Marschner, C.O. Franck, D. Abt, H. Mutlu, C. Barner-Kowollik, Fully independent photochemical reactivity in one molecule, *Chem. Commun.* 55 (2019) 9877–9880, <https://doi.org/10.1039/C9CC04781F>.
- [23] G.B. Veerakanellore, B. Captain, V. Ramamurthy, Solid-state photochemistry of *cis*-cinnamic acids: a competition between [2 + 2] addition and *cis*–*trans* isomerization, *CrystEngComm* 18 (2016) 4708–4712, <https://doi.org/10.1039/C6CE00682E>.
- [24] A. Zanutta, L. Colella, C. Bertarelli, A. Bianco, Understanding the mechanism of refractive index modulation in materials undergoing photo-Fries rearrangement, *Opt. Mater.* 35 (2013) 2283–2289, <https://doi.org/10.1016/j.optmat.2013.06.019>.
- [25] A. Bubnov, M. Cigl, N. Sedláčková, D. Pocięcha, Z. Böhmová, V. Hamplová, Self-assembling behaviour of new functional photosensitive cinnamoyl-based reactive mesogens, *Liq. Cryst.* 47 (2020) 2276–2291, <https://doi.org/10.1080/02678292.2020.1783586>.
- [26] S. Shruthi, M. Smahel, M. Kohout, G. Shanker, G. Hegde, Influence of linking units on the photo responsive studies of azobenzene liquid crystals: Application in optical storage devices, *J. Mol. Liq.* 339 (2021) 116744, <https://doi.org/10.1016/j.molliq.2021.116744>.
- [27] W.A. Skinner, M.G.M. Schelstraete, B.R. Baker, Potential anticancer agents. XLVIII. Analogs of chlorambucil. VI.² Ring isomers, *J. Org. Chem.* 26 (1961) 1554–1557, <https://doi.org/10.1021/jo01064a060>.
- [28] G. Pelzl, S. Diele, A. Jakli, C.h. Lischka, I. Wirth, W. Weissflog, Helical superstructures in a novel smectic mesophase formed by achiral banana-shaped molecules, *Liq. Cryst.* 26 (1999) 135–139, <https://doi.org/10.1080/026782999205641>.
- [29] W. Weissflog, H.N.S. Murthy, S. Diele, G. Pelzl, Relationships between molecular structure and physical properties in bent-core mesogens, *Phil. Trans. R. Soc. A* 364 (2006) 2657–2679, <https://doi.org/10.1098/rsta.2006.1845>.
- [30] W. Weissflog, H. Nádasi, U. Dunemann, G. Pelzl, S. Diele, A. Eremin, H. Kresse, Influence of lateral substituents on the mesophase behaviour of banana-shaped mesogens, *J. Mater. Chem.* 11 (2001) 2748–2758, <https://doi.org/10.1039/B104098G>.
- [31] N.G. Nagaveni, A. Royb, V. Prasad, Achiral bent-core azo compounds: effect of different types of linkage groups and their direction of linking on liquid crystalline properties, *J. Mater. Chem.* 22 (2012) 8948–8959, <https://doi.org/10.1039/C2JM30709j>.
- [32] M. Alaasar, M. Prehm, C. Tschierske, Influence of halogen substituent on the mesomorphic properties of five-ring banana-shaped molecules with azobenzene wings, *Liq. Cryst.* 40 (2013) 656–668, <https://doi.org/10.1080/02678292.2013.767949>.
- [33] M. Alaasar, M. Prehm, C. Tschierske, New azobenzene containing bent-core liquid crystals based on disubstituted resorcinol, *Liq. Cryst.* 41 (2014) 126–136, <https://doi.org/10.1080/02678292.2013.840393>.
- [34] G. Pelzl, S. Diele, S. Grande, A. Jákl, C.h. Lischka, H. Kresse, H. Schmalfluss, I. Wirth, W. Weissflog, Structural and electro-optical investigations of the smectic phase of chlorine-substituted banana-shaped compounds, *Liq. Cryst.* 26 (1999) 401–413, <https://doi.org/10.1080/026782999205182>.
- [35] W. Weissflog, C.h. Lischka, S. Diele, G. Pelzl, I. Wirth, S. Grande, H. Kresse, H. Schmalfluss, H. Hartung, A. Stettler, Banana-shaped or rod-like mesogens? Molecular structure, crystal structure and mesophase behaviour of 4,6-dichloro-1,3-phenylene bis[4-(4-n-subst.-phenyliminomethyl)benzoates], *Mol. Cryst. Liq. Cryst.* 333 (1999) 203–235, <https://doi.org/10.1080/10587259908026006>.
- [36] A. Eremin, H. Nádasi, G. Pelzl, S. Diele, H. Kresse, W. Weissflog, S. Grande, Paraelectric–antiferroelectric transitions in the bent-core liquid-crystalline materials, *Phys. Chem. Chem. Phys.* 6 (2004) 1290–1298, <https://doi.org/10.1039/B312586F>.