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Synthesis and study of new liquid crystalline compounds with an epoxy group

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The influence of the transformation of a terminal double bond to an epoxide group in the series of compounds containing phenyl benzoate moiety as the mesogenic rigid core is investigated. The epoxide derivatives are obtained by biotransformation methods. The double bond or epoxide ring are separated by different numbers of methylene units from the phenyl ring of benzoic acid in its methoxy or decyloxyphenyl esters. The mesogenic properties of the synthesised compounds are investigated by optical microscopy, calorimetric and X-ray methods. In contrast to methoxyphenyl esters most of decyloxyphenyl esters showed enantiotropic liquid crystalline behaviour. The replacement of the double carbon–carbon bond by the polar and bulky epoxy group destabilises the mesophase in almost all cases.

Keywords: nematic phase; smectic phase; liquid crystalline epoxides

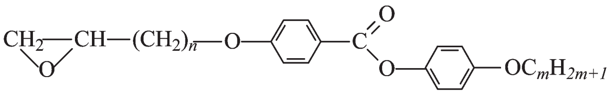
1. Introduction

Liquid crystalline (LC) epoxyresins are of considerable interest owing to their thermoset applications. They have some advantages such as controllable curing rate, high heat and chemical resistance (*1*). Usually they are synthesised from some symmetrical diepoxycompounds cured with 4-aminophenyl 4′-benzoate (DDE) (*2*) or bis-(4-aminophenyl)-methane (DDM) (*3, 4*). Some photopolymerisations of LC diepoxides were realised as well providing the highly ordered polymeric networks (*5*). The diepoxides are generally obtained via oxidation of the appropriate dialkenes by means of 3-chloroperoxybenzoic acid (*1, 2*) or hydrogen peroxide using tetrakis(diperoxotungsto)phosphates as a catalyst in a biphasic system (*6*).

A systematic investigation of the LC properties of dialkenes and diepoxides was carried out by Kaese et al. (*6*). They found that symmetrical epoxides containing three phenyl rings (a dibenzoylhydroquinone structure with lateral substituents in a hydroquinone ring) in general exhibit lower transition temperatures than dialkenes. The temperatures decrease on increasing the length of the methylene spacer (up to four CH_2 units). Some unsymmetrical diepoxides were also obtained and were found to exhibit nematic properties.

However, only few LC monoepoxides have been synthesised and photopolymerised so far (*7*).

The main purpose of this work is the systematic investigation of the influence of epoxidation on the LC properties of substituted phenyl benzoates of general formula:



and to make a comparison with their alkene precursors.

In order to obtain the epoxide terminal group, an enzymatic (hydrogen peroxide, dimethyl carbonate, *Candida antarctica* lipase) method of oxidation of the double bond (*8, 9*) is used. This method has so far only been applied to different hydrocarbons containing double bonds. Here, this type of biotransformation is applied for the first time to compounds with ester functional groups.

2. Experimental details

2.1. Instrumentation

All product structures were confirmed by Fourier transform infrared (FT-IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The IR spectra (in CH_2Cl_2) were recorded on a Perkin-Elmer 2000 apparatus equipped with Pegrams 2000 software, and the NMR spectra (in $CDCl_3$) were recorded using a Varian Gemini 200 MHz spectrometer. The structures were also confirmed by

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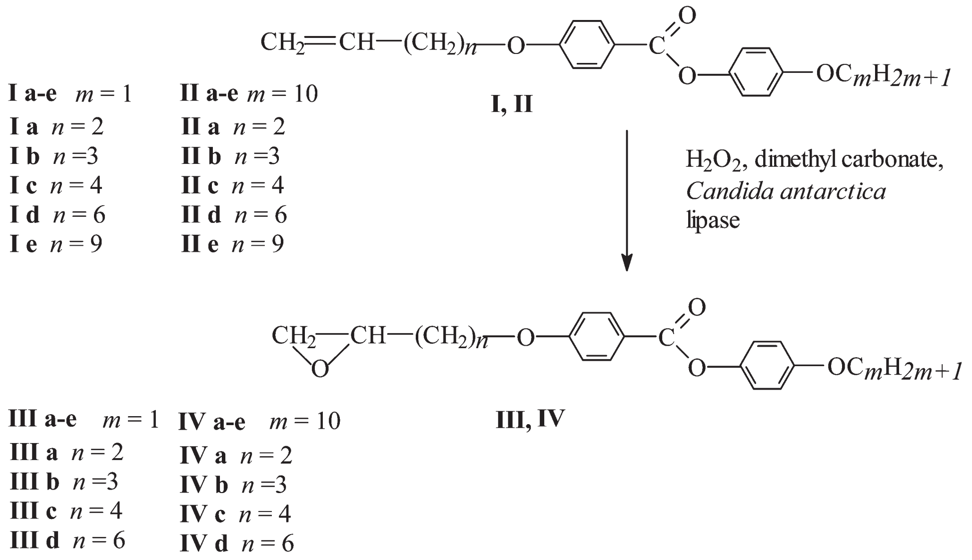
elemental analysis (within ±0.4% of theoretical values). The purity of all compounds obtained was checked by means of a thin-layer chromatography (TLC) method using SiO_2 plates with an ultraviolet (UV) indicator and a chloroform/methanol mixture as an eluent. The X-ray diffraction (XRD) data for LC phases were obtained with a Bruker GADDS system, using CuK_α radiation. The diffractometer was equipped with a Gobel mirror, monocap collimator and two-dimensional HiStar detector. For optical measurements performed with a Nikon Optiphot microscope equipped with a Mettler FP82HT hot stage, 5–6 μm thick glass cell were used. The differential scanning calorimetry (DSC) measurements were performed with a Perkin Elmer 7 calorimeter at a scan rate of $2^\circ C\,min^{-1}$. The molecular lengths were calculated with the Hyperchem 6 work-package. The single-crystal XRD data were collected using the Bruker Kappa APEX-II Ultra controlled by APEX-II software system and equipped with MoKα rotating anode X-ray source, APEX-II CCD detector and a graphite monochromator. The experiment was carried out using the Oxford Cryostream cooling device. A total of 3200 frames of 0.5° oscillation width, divided into 14 phi and omega scans were collected. The generator settings were 50 kV and 100 mA and the crystal to detector distance was set to 40 mm. The exposure time per frame was 20 s. Indexing, integration and initial scaling were performed with *SAINT* and *SADABS* software. The unit cell parameters were obtained and refined based on the whole data sets. The structure was solved by direct methods approach using the *SHELXS-97* program (*10*) and than refinement based on F^2 except reflections with negative intensities was carried out with *SHELXL-97* (*11*). Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the *International Crystallographic Tables Vol. C* (*12*).

2.2. *Synthesis*

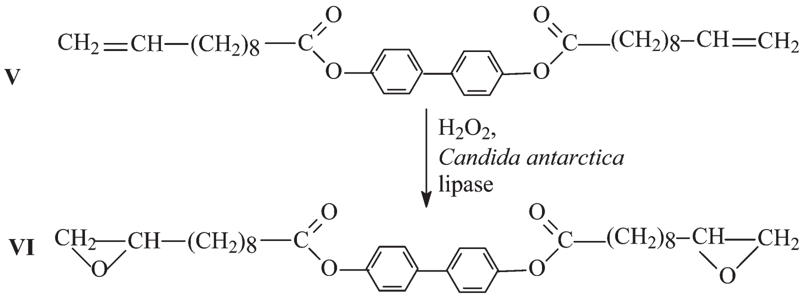
All of the chemicals used were analytical grade commercial products (Sigma-Aldrich) and were applied without further purification. The epoxides were synthesised from the appropriate alkenes according to Schemes 1 and 2.

The 4-alkoxyphenyl esters 4-ω-alkenylobenzoic acid and 4,4′-bis(undecenoiloxy)biphenol were prepared from the appropriate acids and phenols in the presence of *N,N′*-dicyclohexylcarbodiimide and a catalytic amount of *N,N*-dimethyl-4-aminopyridine according to (*13*) and recrystallised from methanol.

The epoxidation was performed according to (*8*). In a typical procedure 0.003 mol of the olefin was dissolved in 30 cm^3 of dimethyl carbonate and 500 mg of lipase acrylic resin from *Candida antarctica* was added. Then over 2 hours 0.015 mol of 50% H_2O_2 was added in small amounts and the mixture was stirred for 48 h in 37°C. The mixture was dried over $MgSO_4$, the solvent was evaporated and the products were purified by column chromatography (SiO_2) using $CHCl_3$–MeOH (50:1) as eluent: the yield was around 30–50%. Typical NMR characterisation results are given for esters (alkenes $m=1$, $n=3$ and 9 and epoxides $m=10$, $n=3$ and 9).



Scheme 1. General route employed for the synthesis of 4-alkoxyphenyl 4′-[(ω-epoxy)alkoxy]benzoates.



Scheme 2. General route employed for the synthesis of 4,4′-biphenyl bis[(10,11-epoxy)undecanoate].

*4-Methoxyphenyl 4′-(pent-4,5-enoxy)benzoate (**Ib**).*

^{1}H-NMR, δ (ppm) 1.40–1.55 (m, 2H, CH_2), 2.25–2.35 (m, 2H, $CH_2{=}CH{-}C\underline{H_2}$), 5.00–5.25 (m, 2H, $CH_2{=}$), 5.80–5.93 (m, 1H, $-CH{=}$), 3.82 (s, 3H, OCH_3), 4.10 (t, 2H, $O{-}CH_2{-}$), 6.90–7.14 (m, 6H, $C{-}H_{arom}$), 8.11–8.16 (m, 2H, $C{-}H_{arom}$).

*4-Methoxyphenyl 4′-(4,5-epoxypentanoxy)benzoate (**IIIb**).*

^{1}H-NMR, δ (ppm) 1.03–1.67 (m, 4H, $(CH_2)_2$), 2.50–2.54 (dd, 1H, C–H, epoxy ring), 2.77–2.82 (dd, 1H, C–H, epoxy ring), 2.97–3.03 (m, 1H, C–H, epoxy ring), 3.82 (s, 3H, OCH_3), 4.10 (t, 2H, $O{-}CH_2{-}$), 6.90–7.14 (m, 6H, $C{-}H_{arom}$), 8.11–8.16 (m, 2H, $C{-}H_{arom}$).

*4-Methoxyphenyl 4′-(undec-10,11-enoxy)benzoate (**Ie**).*

^{1}H-NMR, δ (ppm) 1.30–1.83 (m, 14H, $(CH_2)_7$), 2.00–2.95 (m, 2H, $CH_2{=}CH{-}C\underline{H}_2$), 3.82 (s, 3H, OCH_3), 4.07 (t, 2H, $O{-}CH_2{-}$), 4.90–5.10 (m, 2H, $CH_2{=}$), 5.78–5.89 (m, 1H, $-CH{=}$), 6.70–7.14 (m, 6H, $C{-}H_{arom}$), 8.10–8.15 (m, 2H, $C{-}H_{arom}$).

*4-Methoxyphenyl 4′-(10,11-epoxyundecanoxy)benzoate (**IIIe**).*

^{1}H-NMR, δ (ppm) 1.29–1.85 (m, 16H, $(CH_2)_8$), 2.45–2.49 (dd, 1H, C–H, epoxy ring), 2.72–2.77 (dd, 1H, C–H, epoxy ring), 2.87–2.98 (m, 1H, C–H, epoxy ring), 3.82 (s, 3H, OCH_3), 4.07 (t, 2H, $O{-}CH_2{-}$), 6.90–7.14 (m, 6H, $C{-}H_{arom}$), 8.10–8.15 (m, 2H, $C{-}H_{arom}$).

*4-Decyloxyphenyl 4′-(pent-4,5-enoxy)benzoate (**IIb**).*

^{1}H-NMR, δ (ppm) 0.88 (3H, t, CH_3), 1.03–1.67 (m, 18H, CH_2, $(CH_2)_8$), 2.21–2.32 (m, 2H, $CH_2{=}CH{-}C\underline{H}_2$), 3.98 (t, 2H, $-O\Phi OCH_2{-}$), 4.06 (t, 2H, $-CH_2{-}O\Phi COO{-}$), 5.00–5.25 (m, 2H, $CH_2{=}$), 5.80–5.93 (m, 1H, $-CH{=}$), 6.86–7.12 (m, 6H, $C{-}H_{arom}$), 8.11–8.15 (m, 2H, $C{-}H_{arom}$).

*4-Decyloxyphenyl 4′-(4,5-epoxypentanoxy)benzoate (**IVb**).*

^{1}H-NMR, δ (ppm) 0.88 (3H, t, CH_3), 1.20–2.04 (m, 20H, $(CH_2CH_2$, $(CH_2)_8)$, 2.51–2.54 (dd, 1H, C-H, epoxy ring), 2.77–2.82 (dd, 1H, C–H, epoxy ring), 2.97–3.06 (m, 1H, C–H, epoxy ring), 3.95 (t, 2H, $-O\Phi OCH_2)$, 4.10 (t, 2H, $-CH_2O\Phi COO{-}$), 6.90–7.12 (m, 6H, $C{-}H_{arom}$), 8.11–8.15 (m, 2H, $C{-}H_{arom}$).

*4-Decyloxyphenyl 4′-(undec-10,11-enoxy)benzoate (**IIe**).*

^{1}H-NMR, δ (ppm) 0.887 (3H, t, CH_3), 1.27–1.89 (m, 30H, $((CH_2)_8$, $(CH_2)_7)$, 2.00–2.95 (m, 2H, $CH_2{=}CH{-}C\underline{H}_2$), 3.95 (t, 2H, $-O\Phi OCH_2{-}$), 4.04 (t, 2H, $-CH_2{-}O\Phi COO{-}$), 4.91–5.12 (m, 2H, $CH_2{=}$), 5.75–5.84 (m, 1H $-CH{=}$), 6.89–7.12 (m, 6H, $C{-}H_{arom}$), 8.10–8.15 (m, 2H, $C{-}H_{arom}$).

*4-Decyloxyphenyl 4′-(10,11-epoxyundecanoxy)benzoate (**IVe**).*

^{1}H-NMR, δ (ppm) 0.887 (3H, t, CH_3), 1.27–1.85 (m, 32H, 2 × $(CH_2)_8$), 2.45–2.48 (dd, 1H, C–H, epoxy ring), 2.72–2.77 (dd, 1H, C–H, epoxy ring), 2.87–2.956 (m, 1H, C–H, epoxy ring), 3.95, (t, 2H, $-O\Phi OCH_2{-}$), 4.04 (t, 2H, $-CH_2{-}O\Phi COO{-}$), 6.89–7.26 (m, 6H, $C{-}H_{arom}$), 8.10–8.15 (m, 2H, $C{-}H_{arom}$),

3. Results and discussion

The transition temperatures of alkenes (**Ia–e** and **IIa–e**) and appropriate epoxides (**IIIa–e** and **IVa–e**) are given in Tables 1 and 2, respectively. In addition, the mesogenic ranges of substrates and products are compared in Figures 1 (series **I** and **III**, heating and cooling) and 2 (series **II** and **IV**, heating and cooling).

The thermotropic LC properties of metoxyphenyl esters of alkenyloxybenzoic acid **Ia–e** are rather poor: the mesogenic properties were observed for compounds with long alkenyloxy substituents attached to the mesogenic rigid core. Only the metoxyphenyl esters of octenyloxy (**Id**) and undecenyloxy (**Ie**)

Table 1. Phase transition temperatures (°C) and *enthalpies* (kJ mol^{-1}) for alkenes.

	Heating									Cooling								
Compound	**Cr**		**SmC**		**SmA**		**N**		**Iso**	**Iso**		**N**		**SmA**		**SmC**		**Cr**
Ia	•	53.0	–		–		–		•	•	51.7	•	38.0	–		–		•
		25.1									*−0.37*		*−20.6*					
Ib	•	87.7	–		–		–		•	•	76.4	–						•
		31.3									*−30.5*							
Ic	•	63.8	–		–		–		•	•	60.5	•	49.1	–	–	–		•
		27.1									*−0.37*		*−24.8*					
Id	•	67.5	–		•	75.9	•	84.8	•	•	87.8	•	51.6	•	49.3	–		•
		30.8				*0.30*		*1.89*			*−24.8*		*−2.87*		*−21.3*			
Ie	•	71.5	–		–		•	74.7	•	•	74.6	•	48.6	•	42.2	–		•
		47.5						*0.66*			*−0.67*		*−0.59*		*−34.8*			
IIa	•	58.6	–		–		•	84.9	•	•	86.5	•	45.3	–		–		•
		30.2						*0.65*			*−1.06*		*−24.7*					
IIb	•	61.9	–		–		•	85.4	•	•	85.5	•	56.1	–		–		•
		42.8						*1.47*			*−1.14*		*−28.3*					
IIc	•	54.0	–		•	79.4	•	80.1	•	•	80.4	•	79.3	•	48.3	–		•
		35.2				*0.62*		*0.21*			*−0.18*		*−0.72*		*−20.5*			
IId	•	58.9	–		•	77.5	•	83.6	•	•	83.5	•	77.7	•	34.5	–		•
		41.3				*0.44*		*1.86*			*−1.83*		*−0.72*		*−34.2*			
IIe	•	69.5	•	73.0	•	89.5	–		•	•	89.5	–		•	72.0	•	53.8	•
		50.2				*7.87*					*−7.84*						*−40.7*	

benzoic acid formed enantiotropic LC phase (smectic A and/or nematic). However, in the cooling cycle the monotropic LC phases appeared in all substrates except for pentenyloxy ester (**Ib**). The lack of mesogenic properties in the case of **Ib** is probably due to the odd–even effect, which influences the mesophase temperature range and is particularly pronounced for compounds with short alkenyl tails.

After epoxidation of terminal $CH_2{=}CH$ double bonds the tendency to form the thermotropic LC phase diminishes further: the nematic phase appears only for compound **IIId** with $n{=}6$ during the heating cycle (see Figure 1(a)); on the cooling cycle the occurrence of monotropic phase varied depending on the length of the flexible chain (Figure 1(b)). For $n{=}2$ (compound **IIIa**) the nematic phase of epoxy compound demonstrates higher stability than those for alkenyloxy analogue **Ia**. In the case of $n{=}3$ (compound **IIIb**) only the epoxy compound forms the monotropic nematic phase and for $n{=}4$ (compound

Table 2. Phase transition temperatures (°C) and *enthalpies* (kJ mol^{-1}) for epoxides.

	Heating							Cooling						
Compound	**Cr**		**SmA**		**N**		**Iso**	**Iso**		**N**		**SmA**		**Cr**
IIIa	•	101.5	–		–		•	•	62.4	•	57.1	–		•
		38.2							*−0.31*		*−29.1*			
IIIb	•	95.8	–		–		•	•	73.6	•	66.4	–		•
		33.0							*−0.46*		*−27.4*			
IIIc	•	76.1	–		–		•	•	64.6	•	43.8	–		•
		31.0							*−0.51*		*−27.6*			
IIId	•	63.8	–		•	69.40	•	•	69.3	•	31.3	–		•
		33.4				*0.59*			*−0.67*		*22.1*			
IIIe	•	71.6	–				•	•	70.5	•	49.9	–		•
		46.4							*−1.16*		*−39.8*			
IVa	•	64.6	–		•	81.7	•	•	82.4	•	58.9	•		•
		36.1				*1.07*			*−0.79*		*−32.7*			
IVb	•	68.4	•	75.1	•	84.2	•	•	84.3	•	75.4	•	57.4	•
		43.2		*0.06*		*1.16*			*−1.27*		*−0.09*		*−35.9*	
IVc	•	52.8	•	59.5	•	78.1	•	•	78.1	•	59.6	•	42.0	•
		38.0		*0.01*		*1.40*			*−1.59*		*−0.02*		*−34.2*	
IVd	•	74.8	–		•	79.5	•	•	79.5	•	72.6	•	47.2	•
		70.5				*1.44*			*−1.54*		*−1.54*		*−40.8*	
IVe	•	66.9	•	76.4	•	79.4	•	•	78.9	•	76.8	•	56.6	•
		72.7		*3.45*		*3.77*			*−4.04*		*−4.09*		*−61.7*	

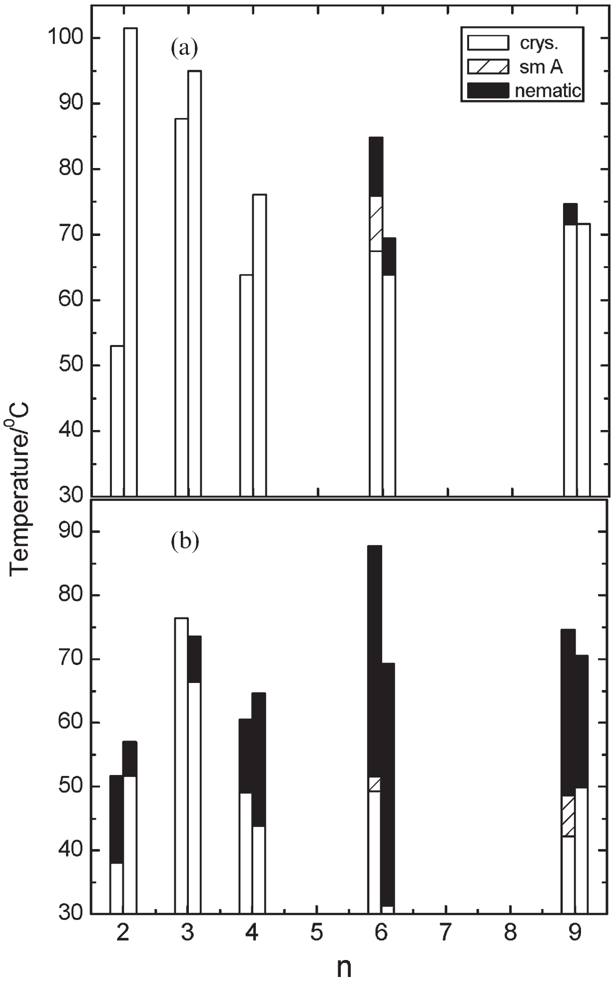


Figure 1. Phase transition temperatures diagrams as a function of the number of methylene groups in the spacer for methoxyphenyl esters, for (a) the heating and (b) the cooling cycle. For each number *n*, the left column corresponds to the substrate (alkenes **Ia–e**) and the right column to the product (epoxides **IIIa–e**).

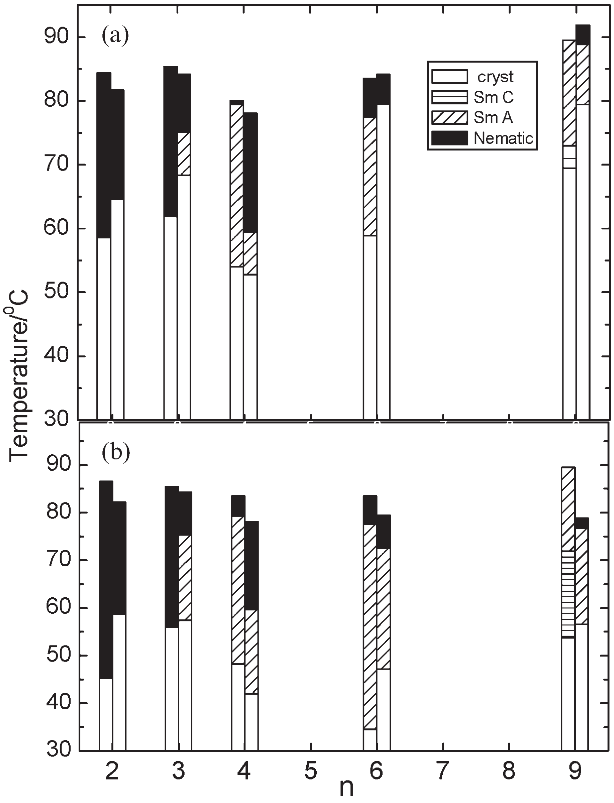


Figure 2. Phase transition temperatures diagrams as a function of the number of methylene groups *n* in the spacer for decyloxyphenyl esters, for (a) the heating and (b) the cooling cycle. For each number *n*, the left column corresponds to the substrate (alkenes **IIa–e**) and the right column to the product (epoxides **IVa–e**).

IIIc) the monotropic nematic phase of epoxy compound has a larger temperature range and stability. From XRD studies it can be deduced that the average distance between molecules (measured along the nematic director direction) in the nematic phase is determined to be about 1.8 nm. For compound **IIIc** the molecular structure was confirmed by a crystallographic method, as this compound forms high-quality crystals. CCDC 709693 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

The unit cell parameters for **IIIc** molecules are given in Table 3. It was found that there is one molecule located at general position in the crystallographic asymmetric unit and there are two antiparallely placed molecules in the crystallographic cell. The structure of the **IIIc** molecule is presented in Figure 3.

The molecule adopts maximally stretched conformation and the molecular length (2.16 nm) is a bit larger than the intermolecular distance found in the nematic phase. In the molecule two phenyl groups are twisted (with twist 67.8°), and the linking ester group is in the plane of inner phenyl rings. Staring from C18 carbon atom of the hydrocarbon tail, the end moiety of the compound is statistically disordered and split into two conformations A and B with occupancies of 0.56 and 0.44, respectively; however, both conformations remain stretched and each has a hydrocarbon chain that is nearly coplanar with the C8–C12 chain of carbon atoms. The presence of large conformational disorder indicates high flexibility of the hydrocarbon–epoxy end group. The observed disorder is also consistent with the rather large thermal displacement ellipsoid observed for some atoms in this end group. We assume that similar molecular core structures should also be observed for other homologues of series **III**.

Table 3. Crystallographic data for compound **IIIc**.

Crystal system, space group	triclinic, P-1
a, b, c (Å)	9.1241(14), 9.6094(14), 11.4952(18)
α, β, γ (°)	68.937(3), 81.001(2), 68.177(3)
Volume (Å^3)	872.8(2)
Number of molecules in unit cell	2
Calculated density (g cm^{-3})	1.295

For longer substituents with n=6 or 9 the stability of the nematic phase diminishes and, in addition, the smectic A phase disappears compared with the appropriate alkenes. The lack of the smectic A phase in epoxy compounds (**IIId, IIIe**) is a consequence of the presence of the bulky epoxy ring at the terminal position, which might disturb the formation of the layers.

In contrast to methoxyphenyl esters all substrates of series **II** and products of series **IV** formed a LC phase. It results from the presence of long flexible substituents at the decyloxyphenyl moiety. All of the compounds of series **II** and **IV** formed the nematic, nematic and smectic or smectic phases (see Figure 2), but the smectic temperature range was shorter (if any) in the epoxy series.

As can be seen in Figure 4, for decyloxyphenyl esters, the alkene with the longest methylene chain (**IIe**) forms the smectic C and A phases, whereas the epoxide analogue (**IVe**) forms only the smectic A phase. The value of the interlayer spacing d and the length of the molecules in the most extended conformation equal to about 3.8 nm are comparable.

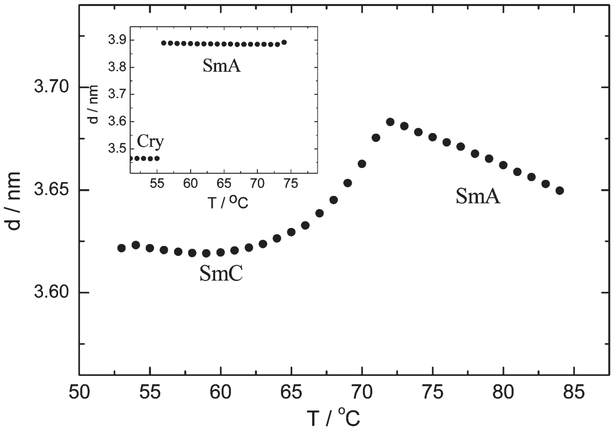


Figure 4. Temperature dependence of the layer thickness, d, for compound **IIe**. Inset: The temperature dependence of the layer thickness, d, for the epoxide analogue, compound **IVe**.

Replacement of the double bond situated at the end of molecule by the bulky and polar epoxide ring with lateral dipole moment makes molecular ordering difficult, especially in the smectic phase. Its influence rises with the length and flexibility of the alkyl chain. As a consequence we observed the diminishing tendency to the formation of higher ordered phases in the series of compounds **IVb–e** compared with alkene analogues.

These tendencies are more pronounced for the symmetrical diesters with a biphenyl group: **V** and **VI**. For substrate **V**, the highly organised smectic X phase is observed for the temperature range 77–111°C (see Figures 5 and 6), whereas its analogues

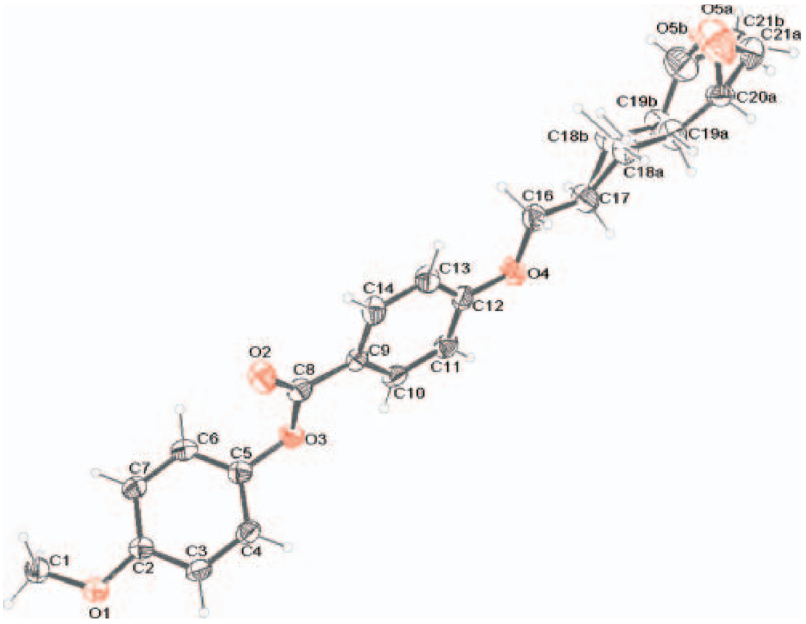


Figure 3. Structure of compound **IIIc** (with the heavy atom numbering scheme). The labels of hydrogens have been omitted for clarity. The thermal ellipsoids are represented at the 50% probability level.

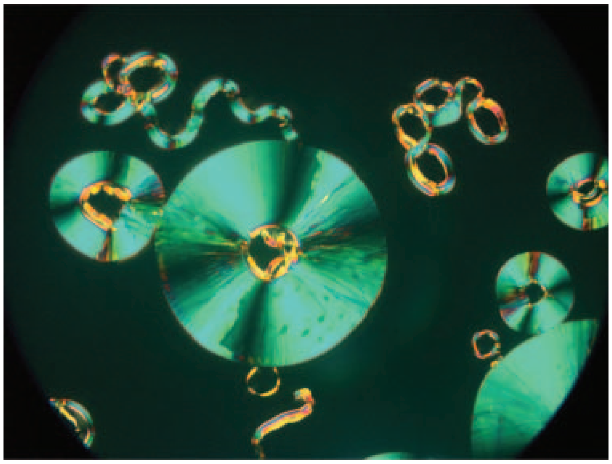


Figure 5. Optical micrographs of the SmX phase of the compound **V** at 109°C after cooling from the isotropic phase.

with two end epoxide groups does not form the LC phase mp. 96°C (Cr-Iso).

To sum up, the mesogenic properties of substrates and products depend on the length of the alkoxy chain between the double bond or epoxy group and the mesogenic core. The only difference between the molecular structure of the substrate and product molecules is the presence of a rigid and unpolar double bond (sp^2 hybridisation of two carbon atoms, and three coplanar carbon atoms as a consequence) in series **I** and **II** and a more flexible, bulky and polar (sp^3 hybridisation of atoms) epoxy ring in series **III** and **IV**. For methoxyphenyl esters (series **I**) only compounds **Id** and **Ie** form the mesophase. It seems, that if the rigid double bond is also close to the polar mesogenic core (compounds **Ia–c**), the molecule cannot reveal mesomorphic character owing to the lack of a flexible part in the molecule, i.e. an alkyl chain of sufficient length. In series **II** the sufficiently long flexible segment (a decyloxy chain attached to a phenyl ring) supplies incompatibility between segments of the molecule, therefore all of the compounds (**IIa–e**) reveal mesogenic character.

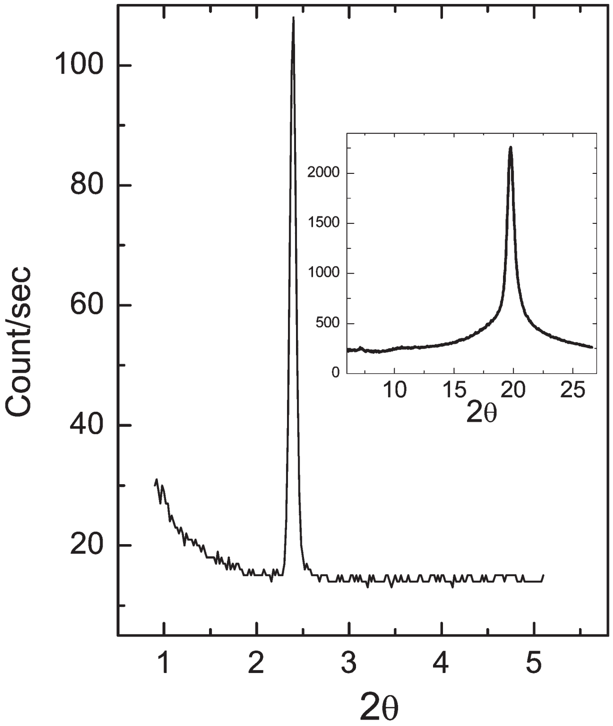


Figure 6. XRD low and high angle (inset) patterns as a function of 2θ angle for the compound **V** taken at 95°C in SmX phase. Inset: Two-dimensional XRD pattern of the high angle signal: the sharpness of the signals reflects the long-range order of molecules in the smectic layer.

4. Conclusions

The *p*-methoxyphenyl esters of *p*-substituted benzoic acid containing an epoxide group show monotropic LC behaviour in contrast to their *p*-decyloxy esters, which are enantiotropic liquid crystals. In both cases the mesogenic properties of the precursors, i.e. alkenyloxyesters, were better, which is particularly relevant in the formation of the smectic phase. The epoxy group, being more polar and bulky than a $CH_2{=}CH{-}$ double bond, destabilises the smectic mesophase in almost all cases.

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