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Syntheses of dialkenes and diepoxides, and the influence of their structural parameters on liquid crystalline properties

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Liquid crystalline dialkenes and diepoxides having different structural parameters were prepared and characterized. The compounds contained two or three aromatic rings in the mesogenic core. The base structure for the compounds containing two aromatic rings is the 4-(ω-oxiranylalkoxy)benzoic acid 4-(ω-oxiranylalkoxy)phenyl ester and for the compounds containing three aromatic rings the 4-{[4-(ω-oxiranylalkoxy)benzoyl]oxy}phenyl 4-(ω-oxiranylalkoxy)benzoate. The hydroquinone moiety is either unsubstituted or contains polar nitrile or fluorine groups as substituents. The flexible spacers consist of different numbers of methylene groups terminated with double bonds or epoxide groups. Some of the diepoxides undergo thermal polymerization of the epoxide group during the determination of the transition temperatures, and therefore the dialkenes were also investigated because of their almost analogous phase behaviour, but with higher thermal stability. Most of the compounds studied show liquid crystalline behaviour. A systematic study is presented of the influence of structural parameters such as the number of aromatic rings in the mesogenic core, substituents and length of the flexible side chain, on the transition temperatures. The diepoxides substituted with polar nitrile or fluorine groups are suitable precursors for ordered network polymers.

1. Introduction

Liquid crystalline monomers for polymerization to ordered polymers and polymer networks are of great interest due to their mechanical and optical properties. By optimizing the chemical structure of the monomers, and by curing or by controlling the polymerization temperature the desired mesophase can be fixed and the polymer properties adjusted [1–6]. In general, the optical properties of ordered polymers with liquid crystalline networks are comparable to those of the low molar mass liquid crystals.

As well as liquid crystalline acrylates [5, 7, 8], methacrylates [6], vinylates [9] and liquid crystalline epoxides [1, 10–18] are also employed in the synthesis of ordered networks. Epoxy resins in general are widely used as adhesives. Possible applications for liquid crystalline epoxides and the resulting polymers include for example adhesives [19], waveguides and mechanically switched optical devices [20]. The formation of polymers having an ordered network structure from diepoxides may be achieved by photopolymerization [1, 10, 11] or by curing with additives such as diamines [15, 20–25].

The present work describes the synthesis and characterization of the liquid crystalline properties of dialkenes and diepoxides consisting of mesogenic units containing two or three aromatic rings, with substitution of the hydroquinone moiety of the mesogenic core by polar nitrile and fluorine groups and flexible spacers of different lengths. The base structures of the compounds synthesized in this work are shown in figure 1. The influence of the different structural parameters on the liquid crystalline properties will be described. In a subsequent paper we will report on the synthesis of network polymers with liquid crystalline superstructures obtained by photopolymerization of the diepoxides. In particular, the compounds containing the polar substituents fluorine and nitrile are interesting because they can be oriented in an electric field due to their negative dielectric anisotropy.

2. Synthesis

The synthesis of liquid crystals containing two or three aromatic rings functionalized with either two alkene

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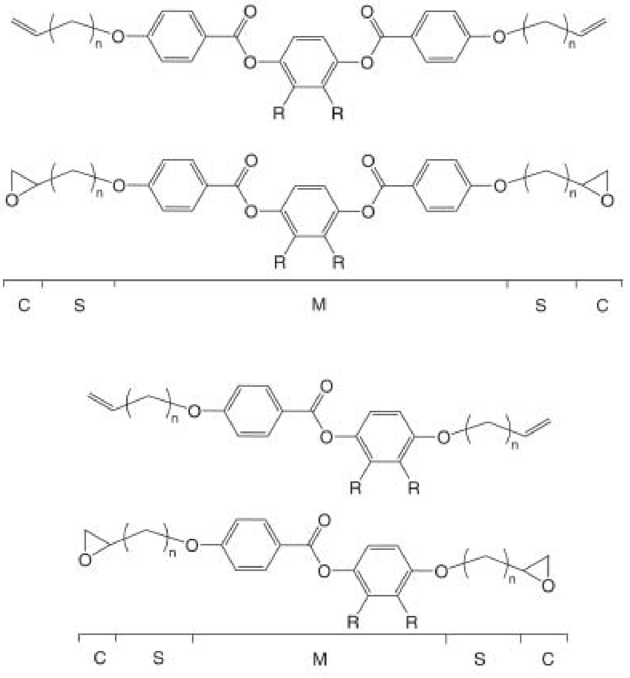


Figure 1. Base structure of the dialkenes and diepoxides prepared, consisting of a mesogenic core (M) containing two or three aromatic rings, flexible spacers (S) and crosslinker (C) [R=−H, −CN, −F; n=1–4].

or two epoxide groups via flexible spacer units are described. Furthermore, the mesogenic core contains different substituents on the hydroquinone moiety, namely hydrogen, nitrile or fluorine. The polar substituents allow for the alignment of the epoxides in an electric field which is at present under investigation, together with the photopolymerization of the diepoxides.

As shown in schemes 1–3 the syntheses of the liquid crystalline dialkenes and diepoxides are accomplished in three steps: (i) the formation of the precursors with one alkenyloxy group for epoxidation and one reactive group for coupling, (ii) the coupling of the precursors to dialkenes, and (iii) the formation of diepoxides. schemes 1–3 contain references to known compounds in square brackets. For all the dialkenes and diepoxides synthesized their mesophase behaviour is listed in table 1. Other analytical data are included in the experimental section.

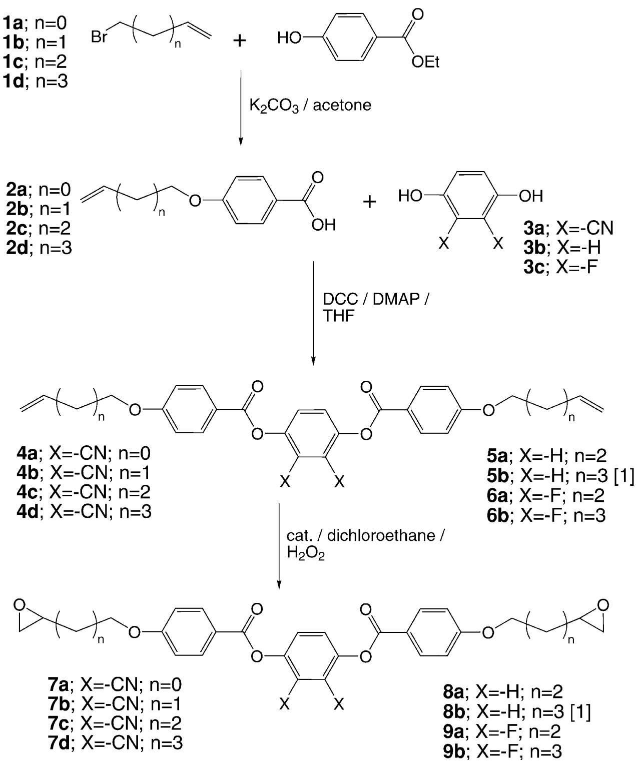
2.1. *Synthesis of the dialkenes and diepoxides containing three aromatic rings*

The precursor ω-bromoalkenes **1a–d** are commercially available or can be prepared as described by Kraus and Landgrebe [26]. The preparation of diepoxides containing three aromatic rings in the mesogenic group started with the synthesis of the precursor ω-alkenyloxybenzoic acid **2** (scheme 1). 4-Hydroxybenzoic acid ethyl ester was reacted with an excess of ω-bromo-alk-1-enes **1a–d** followed by basic hydrolysis of the ethyl esters to give the ω-alkenyloxybenzoic acid **2a–d** (yields 55–75%). In the following reaction these precursors were reacted with 2,3-dicyanohydroquinone (**3a**), hydroquinone (**3b**) and 2,3-difluorohydroquinone (**3c**) in the presence of *N,N'*-dicyclohexyl carbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) to yield the dialkenes **4a–d**, **5a,b**, **6a,b** (yields 14–69%) [27]. The last step of the synthesis was the epoxidation of the dialkenes in 1,2-dichloroethane with hydrogen peroxide as the oxygen source, using tetrakis(diperoxotungsto)phosphates as catalyst in a biphasic system [28, 29] to give **7a–d**, **8a,b**, **9a,b** (yields 57–94%) (scheme 1). This epoxidation system, compared with the normally used *m*-chloroperbenzoic acid, exhibits in our experience the advantages of a faster reaction and an easier purification.

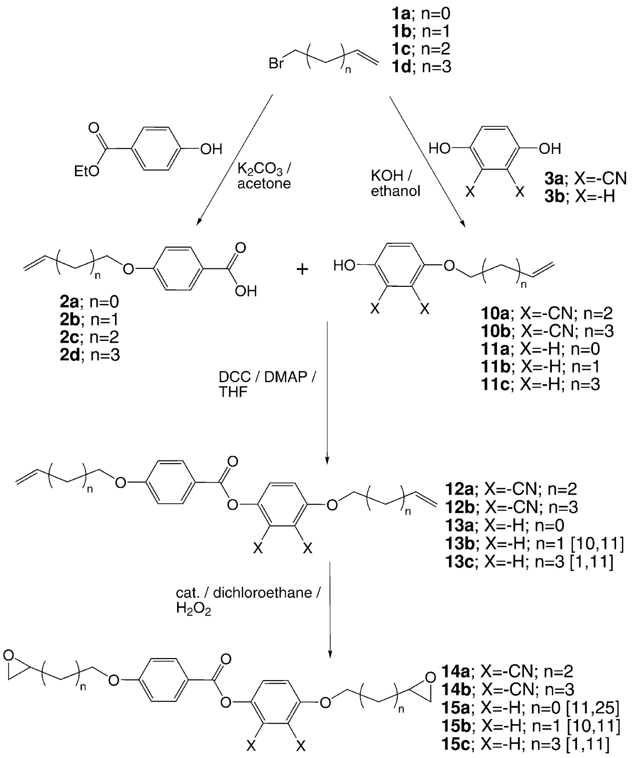
2.2. *Synthesis of the dialkenes and diepoxides containing two aromatic rings*

The preparation of the diepoxides containing two aromatic rings in the mesogenic group was carried out according to the method developed by Broer *et al.* [10]. For the preparation of the diepoxides **14** and **15** the two key precursors ω-alkenyloxybenzoic acid (**2a–d**) and ω-alkenyloxyphenol (**10**, **11**) were synthesized first (scheme 2). The phenolethers **10** and **11** were obtained by the reaction of different ω-bromo-alk-1-enes **1a–d** and an excess of **3a**,**b** (yield 19–72%). The second key precursors **2a–d** were synthesized in yields of 55–75% by the reaction of 4-hydroxybenzoic acid ethyl ester with the ω-bromo-alk-1-enes **1a–d** followed by basic hydrolysis of the ethyl esters. After these reactions the ω-alkenyloxybenzoic acid **2a–d** and the corresponding ω-alkenyloxyphenol **10** and **11** were coupled using DCC and DMAP to give the ω-alkenyloxybenzoic acid ω-alkenyloxyphenyl esters **12** and **13** (yields 54–71%). The following epoxidation of the dialkenes was carried out with the same method as described for the three aromatic ring containing compounds resulting in the diepoxides **14** and **15** (yields 33–94%) (scheme 2). The diepoxides **15a–c** were already described in the literature [1, 10, 11, 25] and are used as reference for the newly prepared substituted diepoxides to show the influence of the nitrile and fluorine groups on mesogenic behaviour.

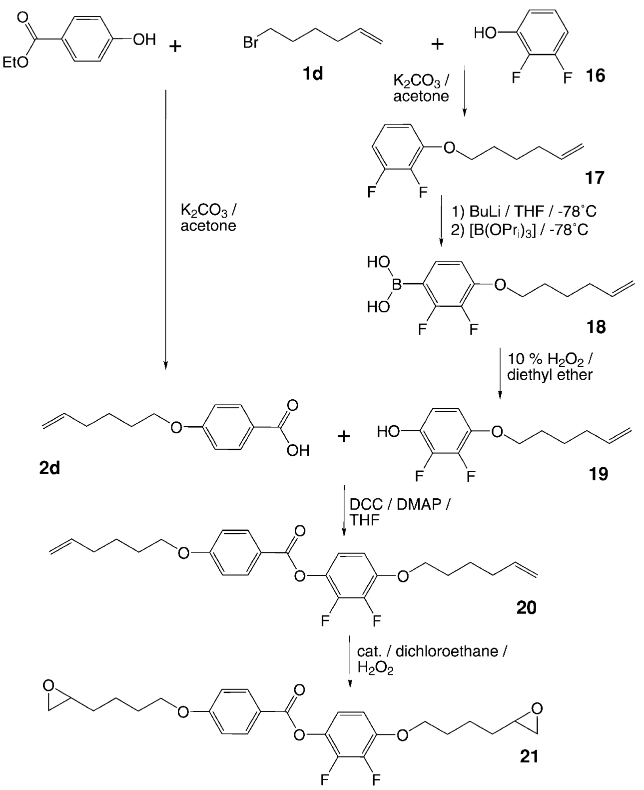
The synthesis of the fluorine substituted phenolether using the method described for the diepoxides containing two aromatic rings was not successful. Therefore an alternative synthetic approach to prepare the fluorinated hydroquinone derivative as the precursor for the fluorinated diepoxide **21** was selected (scheme 3). This precursor was prepared using



Scheme 1. Synthesis of the substituted and unsubstituted dialkenes and diepoxides containing three aromatic rings.



Scheme 2. Synthesis of the substituted and unsubstituted dialkenes and diepoxides containing two aromatic rings.



Scheme 3. Synthesis of the fluorinated dialkene and diepoxide containing two aromatic rings.

2,3-difluorophenol (**16**) as the starting material, which was reacted with 6-bromo-hex-1-ene (**1d**) to give 5-hexenyloxydifluorobenzene (**17**) (yield 93%). Now a second hydroxyl group had to be inserted in the aromatic ring of the ω-alkenyloxydifluorobenzene to give one key precursor. This was realized by adding butyllithium and after a defined reaction time triisopropyl borate to a cooled (−78°C) solution of **17** in THF; subsequent hydrolysis of the 5-hexenyloxydifluorobenzene boronic acid (**18**) with hydrogen peroxide resulted in 5-hexenyloxydifluorophenol (**19**) (yield 82%). The preparation of the second key precursor **2d** has been described already. Now both precursors **2d** and **19** reacted after the addition of DCC and DMAP to the fluorinated dialkene containing two aromatic rings **20** (yield 25%). The last step in the synthesis was the epoxidation of the fluorinated dialkene with the same procedure as described before to give **21** (yield 25%).

3. Thermal characterization and mesophase behaviour

All compounds were examined using differential scanning calorimetry (DSC). The phase behaviour was additionally determined by optical microscopy with polarized light using a hot stage and a (capillary tube) melting point apparatus. All data are included in the experimental part. The results are shown in table 1 and some examples of typical DSC diagrams are shown in figure 2. Some diepoxides show thermal polymerization or decomposition during the DSC measurements, and therefore DSC was also used to characterize all the dialkenes in order to obtain information on the liquid crystalline properties of these compounds which are structurally related to the diepoxides. We found that dialkenes show similar thermal behaviour to diepoxides with regard to the transition temperatures.

3.1. *Dialkenes and diepoxides containing three aromatic rings*

The temperature range in which mesophases are present for the dialkenes with different spacer lengths and nitrile, fluorine and hydrogen substitution are shown in figure 3. The dialkenes **4a–d** containing nitrile groups in the mesogenic core exhibit liquid crystalline behaviour although **4b** and **4d** are monotropic. The melting and clearing points of all four compounds are at temperatures above 100°C. **4d** has the lowest phase transition temperature, compared with the analogous compounds with the melting/clearing point at 143°C. The nematic phase is formed during cooling between 140 and 120°C. The same behaviour is found for compound **4b** with a

Table 1. Phase transition temperatures of the synthesized compounds: () denotes a monotropic transition; Cr=crystalline; N=nematic; S=smectic; I=isotropic phase.

Compound	Temperature and assignment of phase transitions /°C	Enthalpies of phase transitions /kJ mol^{-1}
4a	Cr 182 N 213 I	Cr 37,4 N 2,62 I
4b	Cr 165 I (N 134)	Cr 38,4 I (N 0,7)
4c	Cr 149 N 178 I	Cr 35,0 N 2,96 I
4d	Cr 143 I (N 120)	Cr 32,4 I (N 1,08)
5a	Cr 133 N 227 I	Cr 35,6 N 3,31 I
5b	Cr 125 N 197 I	Cr 37,4 N 2,03 I
6a	Cr 104 N 203 I	Cr 45,4 N 2,41 I
6b	Cr 90 N 177 I	Cr 37,8 N 2,01 I
7a	Cr 124 I [a]	Cr 22,0 I [a]
7b	Cr 144 I [a]	Cr 40,0 I [a]
7c	Cr 110 N 143 I [a]	Cr 19,3 N 1,63 I [a]
7d	Cr 100 I [a]	Cr 21,6 I [a]
8a	Cr 110 S 139 N 235 I	Cr 27,2 S 31,3 N 2,02 I
8b	Cr 116 N 199 I	Cr 30,1 N 1,60 I
9a	Cr 118 N 194 I	Cr 43,6 N 1,71 I
9b	Cr 83 N 150 I	Cr 41,4 N 1,67 I
12a	Cr 86 I (74)	Cr 38,3 I (1,19)
12b	Cr 66 I	Cr 24,0 I
13c	Cr 49 N 62 I	Cr 18,6 N 0,61 I
14a	Cr 73 N 78 I	Cr 24,1 I
14b	Cr 47 ? 81 I [b]	Cr 21,3 ? 32,4 I [b]
15a	Cr 96 I	Cr 26 I
15b	Cr 45 N 61 I	Cr 16,2 N 1,2 I
15c	Cr 40 N 71 I	Cr 19,9 N 1,0 I
20	Cr −40 S 8 N 11 I	Cr 0,98 S 13,7 I
21	Cr 23 S 66 N 67 I	Cr 0,70 S 16 I

[a] Thermal polymerization/decomposition; [b] In addition an exothermal peak was observed at 52°C; ? denotes unknown endothermic phase transition.

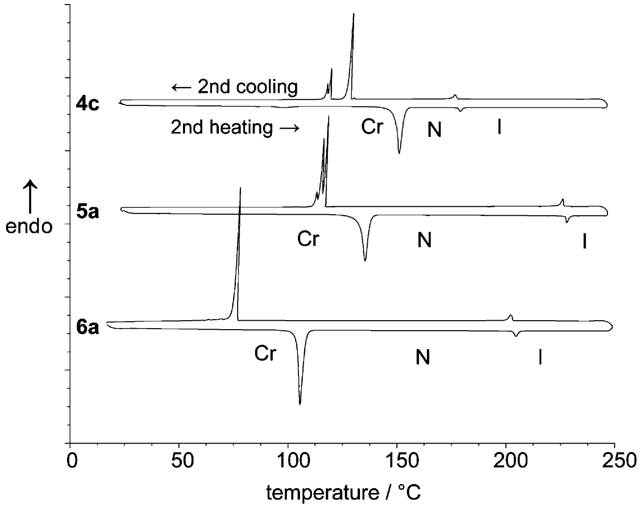


Figure 2. DSC traces of the dialkenes **4c**, **5a** and **6a** containing three aromatic rings (heating rate 10 K min^{-1}).

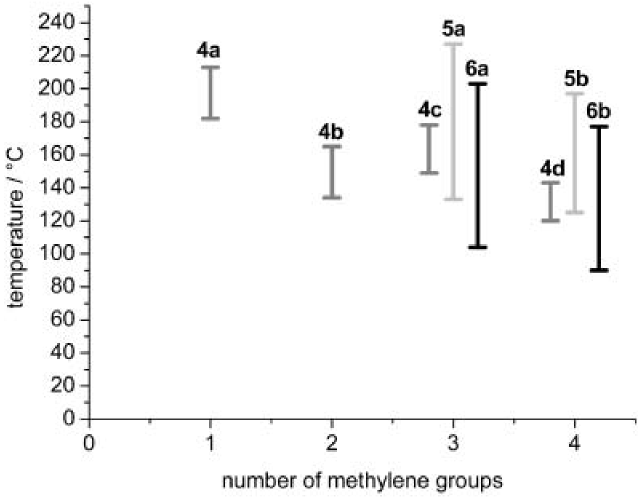


Figure 3. Comparison of the liquid crystalline properties of dialkenes containing three aromatic rings with different mesogenic substitution (light grey, hydrogen substitution; grey, nitrile substitution; black, fluorine substitution).

melting/clearing point at 165°C and on cooling the nematic phase is observed between 154 and 134°C. The behaviour of compounds **4a** and **4c** is different. **4a** exhibits a melting point at 182°C. Above this temperature it shows a nematic mesophase which becomes isotropic at 213°C. **4c** melts at 149°C and clears at 178°C. All four compounds possess the same mesogenic group with different lengths of the alkylene spacer. The transition temperatures decrease as the number of the methylene groups increases. The compounds containing a spacer with an odd number of methylene units have higher transition temperatures than those with an even number [30]. This means that increasing the flexibility of the side chains reduces the transition temperatures, as expected. The dialkenes **5a,b,** with hydrogen instead of the nitrile group in the mesogenic core, show similar behaviour, and the mesophases are stable over a broader temperature range. For example, **5a** (n=2) exhibits a melting point at 135°C and a clearing point as high as 227°C. The compounds **6a,b** containing the fluorinated mesogenic group show crystalline–nematic transitions at lower temperatures than the nitrile-containing and the unsubstituted dialkenes. As with the hydrogen-substituted compounds **5**, a broad mesogenic temperature range is observed. For example, **6b** exhibits a crystal–nematic transition at 90°C and the clearing point at 177°C.

Substitution on the mesogenic core of the dialkenes containing three aromatic rings has a significant influence on the mesogenic properties. The –CN substituents, being rather large, reduce the length to breadth ratio of the molecule. A smaller temperature range over which the mesophase is stable was observed. In contrast the smaller substituents hydrogen and fluorine result in a broad mesogenic temperature range (figures 2 and 3). The fluorine compounds show the lowest transition temperatures and the broadest mesophase, which may be explained by a charge-transfer interaction.

Most diepoxides exhibit liquid crystalline properties. In some cases, especially with the nitrile substituted compounds **7**, the transition temperatures of the diepoxides are difficult to measure by DSC due to the thermal polymerization of the epoxide groups occurring at higher temperatures. All diepoxides **7a–d**, bearing nitrile substituents in the mesogenic core, show an irreversible thermal transition at a relatively high temperature, which is due to the polymerization of the epoxide groups. **7a**, **7b**, and **7d** exhibit only broad peaks in the DSC during heating. Either small peaks without assignment or no peaks occur in the cooling run and in the subsequent second heating run. **7c** is the only compound which shows more than one broad signal in the DSC. The compound melts at about 110°C and exhibits an isotropic transition temperature at 143°C (figure 4). No phase transitions are detected in the cooling run. This indicates that in this case also an irreversible change takes place during heating. In contrast, the diepoxides substituted with hydrogen (**8a,b**) or with fluorine (**9a,b**) exhibit sharply defined thermal transitions and broad mesogenic temperature ranges in the DSC measurements. Compound **8a,** with the shorter flexible spacer (n=2), forms a mesophase at 110°C, which appears to be a smectic phase as observed by polarising microscopy. The nematic phase begins at 139°C and finally **8a** has a clearing point at 235°C. **8b** shows the phase transition from crystalline to nematic at 116°C and to isotropic at 199°C (figure 4). As in the case of the dialkenes, compounds **9a,b** with fluorine substituents on the mesogenic group are characterized by low transition temperatures to the mesophase and by broad temperature ranges. The thermal transitions from the crystal to nematic for **9a,b** are at 118 and 83°C and the clearing points are 194 and 150°C, respectively. Thus these decrease with increasing number of methylene groups in the spacer (figure 4).

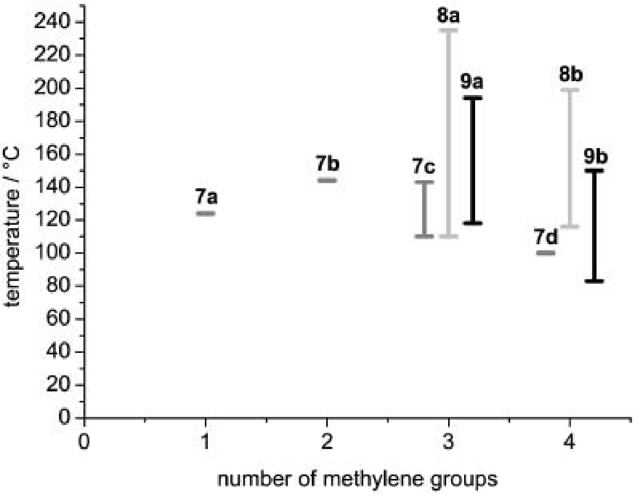


Figure 4. Comparison of the liquid crystalline properties of diepoxides containing three aromatic rings with different mesogenic substitution (light grey, hydrogen substitution; grey, nitrile substitution; black, fluorine substitution).

A comparable behaviour was found for the diepoxides as for the dialkenes. Some nitrile-substituted diepoxides undergo thermal polymerization. Unsubstituted and fluorine-substituted diepoxides show broad mesogenic temperature ranges with relatively low transitions from the crystal to the liquid crystal state.

3.2. *Dialkenes and diepoxides containing two aromatic rings*

Dialkenes **12** containing nitrile substituents were synthesized only with longer side chains (n=2, 3), because in our experience the hydrogen substituted compounds with shorter flexible spacers (n=0, 1) exhibit only monotropic properties. The dialkene **12a** shows monotropic behaviour with a broad melting peak at 86°C, and the formation of a nematic phase between 74 and 63°C on cooling. **12b** on the other hand shows no liquid crystalline phase, melting at 66°C and recrystallizing at 42°C. To illustrate the behaviour of the hydrogen-substituted dialkenes **13**, the mesophase behaviour of one compound is given. Thus, **13c** forms a nematic phase at 49°C and clears at 62°C. The fluorine substituted compound **20** is a low melting substance. It is a viscous liquid at room temperature and exhibits interesting phase transition properties (figure 5). The compound shows a glass temperature at −60°C and a smectic phase at about −40°C. Furthermore the compound forms a nematic phase but the phase transition temperatures are very close so that only one peak with a shoulder is observed at 11°C.

For most diepoxides containing two aromatic rings mesogenic properties are observed. The nitrile-substituted diepoxides **14a,b** show liquid crystalline behaviour. **14a** shows a melting peak at 73°C with a relatively large shoulder at 78°C which is probably the clearing peak, indicating the presence of a mesophase over a small temperature range (figure 6). Compound **14b** exhibits exothermic and endothermic peaks in the DSC trace. The first endothermic peak appears at 47°C and directly after this an exothermic peak begins at 52°C. The second endothermic peak is found at 81°C.

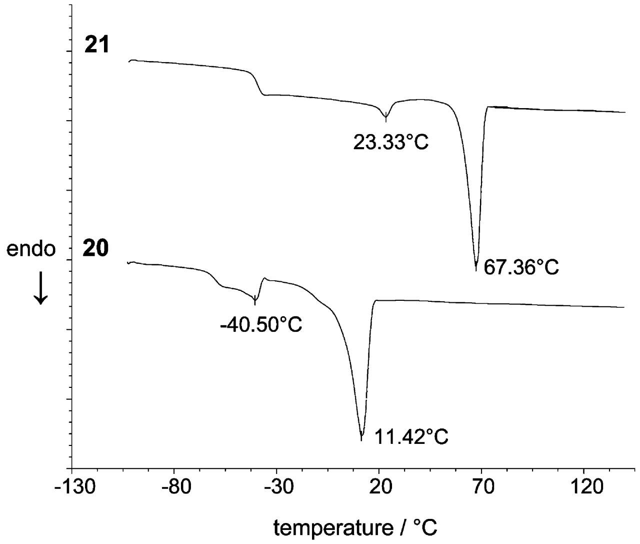


Figure 5. DSC traces of compounds **20** and **21** (heating rate 3 K min^{-1}).

The exothermic peak is difficult to explain and needs further investigation. The compounds **15a–c** containing an unsubstituted hydroquinone moiety in the mesogenic group have been already described elsewhere [1, 10, 11, 19]. Their mesogenic behaviour is mentioned for comparison (table 1, figure 6). These compounds **15a–c** show either monotropic behaviour (**15a**) or exhibit lower transition temperatures (**15b,c**) compared with the nitrile substituted compounds. The fluorine substituted diepoxide **21** shows analogous behaviour to its precursor **20.** The compound possesses a glass temperature at −39°C and a smectic phase is formed at 23°C. The clearing point is 67°C with a smectic–nematic phase transition observed at 66°C as a shoulder (figure 5). Comparing the diepoxides **14b**, **15c** and **21** (n=3), it is clearly seen that the transition temperatures decrease in the order **14b**>**15b**>**21**.

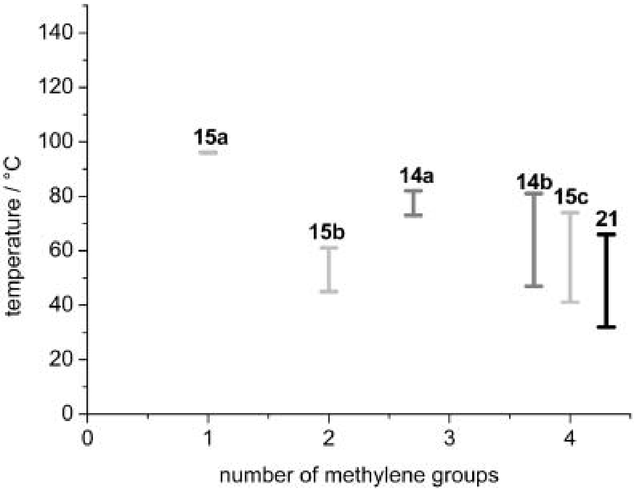


Figure 6. Comparison of the liquid crystalline properties of diepoxides containing two aromatic rings with different mesogenic substitution (light grey, hydrogen; grey, nitrile; black, fluorine).

3.3. *Comparison of the mesogenic behaviour of dialkenes and diepoxides*

The phase transition temperatures of the dialkenes and diepoxides examined are similar in all cases. This is shown in figure 7 in which the transition temperatures (crystal → liquid crystal and liquid crystal → isotropic) of the diepoxides are compared with those of the corresponding dialkenes having the same number of methylene groups in the flexible spacers (for the values of the transition temperatures see table 1). For identical transition temperatures of the corresponding dialkenes and diepoxides the regression line would be the bisectrix, i.e. if the diepoxides and the dialkenes have identical thermal behaviour. As seen in figure 6, the diepoxides have similar but slightly lower transition temperatures than the dialkenes but show in most cases the same phases.

4. Conclusions

Several dialkenes and diepoxides containing two or three aromatic rings in the mesogenic groups were successfully synthesized in good yields. The hydroquinone moiety in the mesogenic group is either unsubstituted or contains nitrile or fluorine as substituents. The variation of aromatic rings in the mesogenic core, the substituents on the mesogenic group and the number of methylene groups in the spacer allow us to

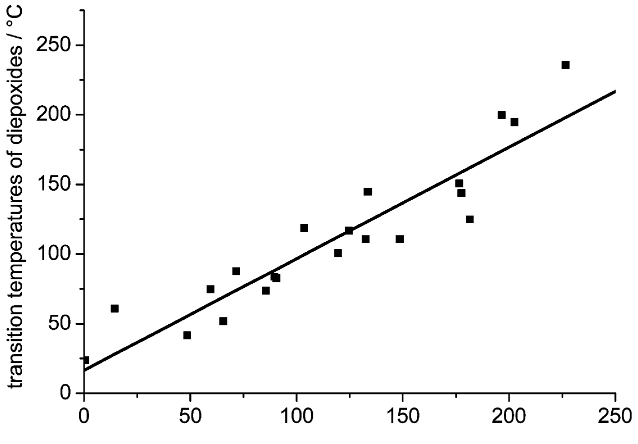


Figure 7. Comparison of the transition temperatures of diepoxides with dialkenes (black line is the linear regression).

study the influence of these structural parameters on the liquid crystalline behaviour.

The observed are:

(a) All the transition temperatures for the compounds containing three aromatic rings are, as expected, higher than those containing two aromatic rings.
(b) The diepoxides exhibit slightly lower transition temperatures than the dialkenes.
(c) On increasing the number of methylene groups in the flexible spacer, the transition temperatures decrease, and alternate according to parity.
(d) Compared with the nitrile substituted compounds, the unsubstituted and fluorine substituted compounds show mesophases stable over much broader temperature ranges.
(e) In most cases the fluorine substituted compounds exhibit the lowest transition temperatures for the crystal to liquid crystal phase change.
(f) Most diepoxides containing three aromatic rings with nitrile substitution have no liquid crystalline properties. Thermal polymerization occurs during the heating run of the DSC measurements due to the high transition temperatures.

The fluorine- and nitrile-substituted diepoxides have dipole moments perpendicular to the molecular long axis, which results in a negative dielectric anisotropy [31–33]. Therefore these compounds are interesting for the preparation of ordered networks due to the low transition temperatures and the broad mesogenic temperature ranges, especially of the fluorine substituted diepoxides. In a subsequent paper we will report in detail on the photopolymerization of these compounds in an electric field with the aim of preparing polymers with a liquid crystalline superstructure.

5. Experimental part

5.1. *Characterizations*

The IR spectra were recorded with a Perkin Elmer SP1000, the MS spectra with a MAT Finigan and the ^{1}H NMR spectra with a Bruker 360. DSC measurements were carried out with a TA Instruments 2920 modulated DSC. The phase transition behaviour of the monomers was investigated using a heating and cooling rate of 10 K min^{-1}. Temperature modulation was used if a separation between reversible and non-reversible effects was required. In these cases heating and cooling rates were 3 K min^{-1}. Polarization microscopic investigations of the compounds were carried out with an Olympus SZ40 polarization microscope with heating stage in order to obtain information about the type of mesogenic phase.

5.2. *Synthesis of the precursors*

If not otherwise mentioned solvents and chemicals were used as commercially received. All bromoalkenes employed are commercially available (Aldrich) or can be prepared as described by Kraus and Landgrebe [26]. The esters **4**, **5**, **6**, **12**, **13**, **20** were prepared analogously to a method described in the literature [1, 10, 27]. Spectroscopic data of structurally analogous compounds are presented only for one compound of each homologous series.

5.2.1. 4-(Allyloxy)benzoic acid (2a), 4-(but-3-enyloxy)benzoic acid (2b), 4-(pent-4-enyloxy)benzoic acid (2b) and 4-(hex-5-enyloxy)benzoic acid (2d). A mixture of 0.075 mol ethyl 4-hydroxybenzoate, 0.094 mol of the bromoalkene **1**, 15.9 g K_2CO_3 and 100 ml acetone was heated under reflux for 24 h. After filtration the solvent was evaporated and 100 ml diethyl ether and 50 ml water were added. Then the phases were separated and the etheric phase extracted twice with 50 ml 10% aqueous NaOH. After evaporation of the diethyl ether, the remaining crude product was heated under reflux with a 150 ml ethanol/water mixture (ratio 1/2) containing 12.2 g KOH until a clear solution was obtained. The solution was then cooled and acidified with 6N HCl to pH 2. The precipitated product was filtered and washed for 30 min with 150 ml water. Yields: **2a** 55%, **2b** 73%, **2c** 75%, **2d** 75%.

2d: FTIR (KBr pellet) ν (cm^{-1}): 3078, 2933, 2875, 2662, 2543, 1677, 1605, 1576, 1514, 1469, 1429, 1393, 1321, 1296, 1259, 1168, 1128, 1110, 1048, 1011, 951, 919, 849, 774, 698, 648, 550, 514. MS (EI, 70 eV, direct inlet 200°C) *m/z* (rel. intensity in %): 220 (55), 192 (60), 138 (56), 121 (100). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.96 (m, 2H), 7.00 (m, 2H), 5.83 (qt, 1H), 5.00 (m, 2H), 4.08 (t, 2H), 2.07 (m, 2H), 1.80 (m, 2H), 1.58 (m, 2H).

5.2.2. 2,3-Difluorohydroquinone (3c). A solution of 14.60 g (58.26 mmol) boron tribromide in dichloromethane was added dropwise to 3.38 g (19.42 mmol) 4-ethoxy-2,3-difluorophenol in 50 ml dry dichloromethane at 0°C and then heated for 1 h under reflux. Afterwards the solution was poured into 100 ml water and 100 ml diethyl ether was added. The precipitate was filtered off and the organic phase extracted with 50 ml 2N KOH. The aqueous solution was acidified with 6N HCl and again extracted with diethyl ether. After drying over $MgSO_4$ and evaporation of the solvent, 2.7 g (95%) 2,3-difluorohydroquinone **3c** was obtained. FTIR (KBr pellet) ν (cm^{-1}): 3305, 2937, 2856, 1624, 1517, 1504, 1419, 1362, 1313, 1277, 1260, 1233, 1199, 1168, 1041, 977, 808, 757, 678, 565, 479. MS

(EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. intensity in %): 146 (100), 98 (20), 70 (27). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.65 (d, 2H).

5.2.3. 3-(Pent-4-enyloxy)-6-hydroxyphthalonitrile (10a), 3-(hex-5-enyloxy)-6-hydroxyphthalonitrile (10b), 4-(allyloxy)phenol (11a), 4-(but-3-enyloxy)phenol (11b) and 4-(hex-5-enyloxy)phenol (11c). To a boiling solution of 0.497 mol hydroquinone or 2,3-dicyanohydroquinone and 0.251 mol α,ω-bromoalkene **1** in 130 ml ethanol, a solution of 25 g KOH in 70 ml H_2O was added dropwise over a period of 4 h. After heating under reflux for 18 h the solution was poured into ice water (400 ml H_2O/ 200 g ice). The mixture was extracted twice with 100 ml diethyl ether, and the ether phases were washed twice with 100 ml 10% aqueous KOH. The combined water phases were again extracted with 100 ml diethyl ether and then acidified with 6N HCl. The mixture was extracted twice with 60 ml dichloromethane. The organic phases were treated with 50 ml of a saturated aqueous NaCl solution and dried over $MgSO_4$. The solvent was evaporated and the remaining crude product purified by column chromatography over silica gel (solvent: chloroform). Yields: **10a** 43%, **10b** 72%, **11a** 25%, **11b** 18%, **11c** 15%.

10b: FTIR (KBr pellet) *v* (cm^{-1}): 3077, 2979, 2883, 2247, 2234, 1647, 1584, 1500, 1459, 1445, 1417, 1387, 1347, 1297, 1264, 1181, 1112, 1040, 989, 927, 824, 754, 668, 626, 571, 514, 469. MS (EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. intensity in %): 192 (20), 110 (100). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.8 (m, 4H), 5.9 (m, 1H), 5.1 (m, 2H), 4.0 (t, 2H), 2.1 (m, 2H), 1.5 (m, 4H).

5.2.4. 1,2-Difluoro-3-(hex-5-enyloxy)benzene (17). A solution of 6.52 g (0.04 mol) 1,5-bromohexene in 20 ml acetone was added dropwise to a stirred mixture of 5 g (0.038 mol) 2,3-difluorophenol (**16**) and 11.06 g (0.080 mol) K_2CO_3 in 50 ml acetone at room temperature. While stirring, the mixture was heated under reflux until TLC analysis revealed a complete reaction. (TLC plastic sheets, 0.2 mm silica gel with fluorescent indicator for 254 nm/dichloromethane.) The crude product was extracted twice with 40 ml diethyl ether and dried with Na_2SO_4. The solvent was removed in vacuum and the crude product was purified by column chromatography over silica with dichloromethane as solvent to give 8 g (93 %) of **17**. FTIR (KBr pellet) *v* (cm^{-1}): 3078, 2942, 2875, 1620, 1597, 1515, 1482, 1440, 1416, 1392, 1318, 1292, 1254, 1223, 1168, 1077, 994, 952, 913, 818, 766, 723, 706. MS (EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. intensity in %): 212 (10) [M], 130 (80), 82 (71), 67 (65), 55 (100), 41 (72). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.0 (m, 1H), 6.74 (m, 2H), 5.8 (m, 1H), 5.0 (m, 2H), 4.0 (t, 2H), 2.15 (q, 2H), 1.9 (m, 2H), 1.6 (m, 2H).

5.2.5. 1,2-Difluoro-3-(hex-5-enyloxy)phenylboronic acid (18). 2.21 ml (22.10 mmol) n-butyllithium (10M in hexane) was added dropwise to a stirred, cooled (−78°C) solution of 4.25 g (20.1 mmol) 2,3-difluoro-1-hexenoxybenzene (**17**) in 30 ml dry THF in a dry nitrogen atmosphere. The reaction mixture was stirred for 3 h, then a previously cooled (−78°C) solution of 7.55 g (40.1 mmol) triisopropyl borate in 20 ml dry THF was added dropwise at −78°C. The reaction was allowed to warm to room temperature overnight then stirred for about 1 h with HCl (10%, 30 ml). The product was extracted twice with 30 ml diethyl ether, and then the combined ether extracts were washed with water and dried with $MgSO_4$. The solvent was evaporated and the crude product purified by column chromatography over silica with dichloromethane as solvent. Yield: 5.15 g (99%). FTIR (KBr pellet) *v* (cm^{-1}): 3331, 3078, 2938, 2863, 1626, 1574, 1519, 1467, 1362, 1305, 1223, 1164, 1130, 1079, 1033, 900, 817, 788, 745, 731, 663, 625, 562. MS (EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. intensity in %): 468 (60), 256 (20) [M], 174 (100), 83 (66), 67 (26), 55 (95), 41 (67). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.4 (m, 1H), 6.95 (m, 1H), 5.8 (m, 1H), 5.0 (m, 2H), 4.1 (m, 2H), 2.15 (m, 2H), 1.8 (m, 2H), 1.6 (m, 2H).

5.2.6. 1,2-Difluoro-3-(hex-5-enyloxy)phenol (19). 15.21 ml hydrogen peroxide (10%, 50.5 mmol) was added dropwise to a stirred solution of 3.3 g (12.89 mmol) **18** in 20 ml diethyl ether, and then heated under reflux for 2.5 h. After cooling, the etheric phase was separated and the aqueous layer extracted twice with 20 ml diethyl ether. The combined ether phases were washed with 10% aqueous sodium hydroxide (4 × 10 ml) and then the separated aqueous phases were acidified with 6N HCl. The product was extracted from the aqueous phase into dichloromethane (3 × 20 ml) and the combined dichloromethane phases were washed with water and dried over $MgSO_4$. The solvent was removed in vacuum to give 2.41 g (82%) **19**. FTIR (KBr pellet) *v* (cm^{-1}): 3401, 3078, 2942, 2873, 1641, 1610, 1513, 1504, 1471, 1456, 1435, 1416, 1392, 1276, 1196, 1170, 1080, 1022, 942, 913, 864, 795, 756, 730, 701, 632, 609. MS (EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. intensity in %): 228 (10) [M], 146 (100), 83 (10), 67 (5), 55 (40), 41 (20). ^{1}H NMR ($CDCl_3$) δ (ppm): 6.52 (m, 2H), 5.8 (m, 1H), 5.05 (m, 2H), 4.02 (m, 2H), 2.15 (m, 2H), 1.83 (m, 2H), 1.60 (m, 2H).

5.3. *Synthesis of the diepoxides containing three aromatic rings*

5.3.1. 2,3-Dicyano-4-{[4-(allyloxy)benzoyl]oxy}phenyl4-(allyloxy)benzoate (4a), 2,3-dicyano-4-{[4-(but-3-enyloxy)benzoyl]oxy}phenyl 4-(but-3-enyloxy)benzoate (4b), 2,3-dicyano-4-{[4-(pent-4-enyloxy)benzoyl]oxy}phenyl 4-(pent-4-enyloxy)benzoate (4c), 2,3-dicyano-4-{[4-(hex-5-enyloxy)benzoyl]oxy}phenyl 4-(hex-5-enyloxy)benzoate (4d), 4-{[4-(pent-4-enyloxy)benzoyl]oxy}phenyl 4-(pent-4-enyloxy)benzoate (5a), 2,3-difluoro-4-{[4-(hex-5-enyloxy)benzoyl]oxy}phenyl 4-(hex-5-enyloxy)benzoate (5b), 2,3-difluoro-4-{[4-(pent-4-enyloxy)benzoyl]oxy}phenyl 4-(pent-4-enyloxy)benzoate (6a) and 2,3-difluoro-4-{[4-(hex-5-enyloxy)benzoyl]oxy}phenyl 4-(hex-5-enyloxy)benzoate (6b). A mixture of 19.2 mmol alkenyloxybenzoic acid (**2a–d**), 9.6 mmol hydroquinone derivative (**3a**, **3b** or **3c**), 20 mmol DCC and 2 mmol DMAP in 50 ml tetrahydrofuran or diethyl ether were stirred for 6 h at room temperature. The precipitate formed was filtered off and the solution washed three times with 100 ml water, 100 ml 5% acetic acid and again 100 ml water. After separation of the organic phase and evaporation of the solvent the residue was purified by column chromatography (silica gel/dichloromethane). Yields: **4a** 43%, **4b** 45%, **4c** 45%, **4d** 49%, **5a** 69%, **5b** 14%, **6a** 43%, **6b** 50%.

4a: FTIR (KBr pellet) ν (cm^{-1}): 3083, 2920, 2239, 1744, 1651, 1606, 1581, 1511, 1479, 1423, 1318, 1264, 1225, 1168, 1120, 1059, 1007, 934, 887, 844, 758, 689, 668. MS (EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. Intensity in %): 480 (4) [M], 161 (100), 121 (31), 41 (30). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.10 (m, 4H), 7.20 (m, 6H), 6.00 (m, 2H), 5.20 (m, 4H), 4.65 (m, 4H).

5.3.2. 2,3-Dicyano-4-({4-[(oxiran-2-yl)methoxy]benzoyl}oxy)phenyl 4-[(oxiran-2-yl)methoxy]benzoate (7a), 2,3-dicyano-4-({4-[2-(oxiran-2-yl)ethoxy]benzoyl}oxy)phenyl 4-[2-(oxiran-2-yl)ethoxy]benzoate (7b), 2,3-dicyano-4-({4-[3-(oxiran-2-yl)propoxy]benzoyl}oxy)phenyl 4-[3-(oxiran-2-yl)propoxy]benzoate (7c), 2,3-dicyano-4-({4-[4-(oxiran-2-yl)butoxy]benzoyl}oxy)phenyl 4-[4-(oxiran-2-yl)butoxy]benzoate (7d), 4-({4-[3-(oxiran-2-yl)propoxy]benzoyl}oxy)phenyl 4-[3-(oxiran-2-yl)propoxy]benzoate (8a), 4-({4-[4-(oxiran-2-yl)butoxy]benzoyl}oxy)phenyl 4-[4-(oxiran-2-yl)butoxy]benzoate (8b), 2,3-difluoro-4-({4-[3-(oxiran-2-yl)propoxy]benzoyl}oxy)phenyl 4-[3-(oxiran-2-yl)propoxy]benzoate (9a) and 2,3-difluoro-4-({4-[4-(oxiran-2-yl)butoxy]benzoyl}oxy)phenyl 4-[4-(oxiran-2-yl)butoxy]benzoate (9b). To 20 ml 1,2-dichloroethane in a 100 ml flask equipped with mechanical stirrer, thermometer and reflux condenser 2.25 mmol of the appropriate olefin (**4a–d**, **5a**, **5b**, **6a** or **6b**) and 0.03 mmol tetrakis(diperoxotungsto)phosphate [18, 19] was added. Then, 10 ml 16% (24 mmol) H_2O_2 was introduced. The resultant biphase mixture was heated at 70°C for the required (about 15 h) time to complete the reaction (TLC reaction control). The water and organic phase were separated and after evaporation of the organic solvent the remaining crude product was chromatographed over silica gel using dichloromethane as eluent. Yields: **7a** 94%, **7b** 94%, **7c** 76%, **7d** 93%, **8a** 57%, **8b** 84%, **9a** 75%, **9b** 59%.

7a: FTIR (KBr pellet) ν (cm^{-1}): 3081, 3005, 2930, 2238, 1748, 1606, 1512, 1480, 1422, 1318, 1265, 1227, 1170, 1060, 1024, 914, 885, 844, 804, 775, 688. MS (EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. intensity in %): 512 (2) [M], 335 (16), 177 (100), 160 (15), 121 (43), 57 (13). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.11 (m, 4H), 7.10 (m, 6H), 4.03 (m, 4H), 3.04 (m, 2H), 2.50 (m, 4H).

5.4. *Synthesis of the diepoxides containing two aromatic rings*

5.4.1. 2,3-Dicyano-4-(pent-4-enyloxy)phenyl 4-(pent-4-enyloxy)benzoate (12a), 2,3-dicyano-4-(hex-5-enyloxy)phenyl 4-(hex-5-enyloxy)benzoate (12b), 4-(allyloxy)phenyl 4-(allyloxy)benzoate (13a), 4-(but-3-enyloxy)phenyl 4-(but-3-enyloxy)benzoate (13b), 4-(hex-5-enyloxy)phenyl 4-(hex-5-enyloxy)benzoate (13c) and 2,3-difluoro-4-(hex-5-enyloxy)phenyl 4-(hex-5-enyloxy)benzoate (20). A mixture of 9.6 mmol alkenyloxybenzoic acid (**2a–d**), 9.6 mmol of an alkenyloxyphenol (**10a, 10b**, **11a–c** or **19**), 10 mmol DCC and 1 mmol DMAP in 50 ml THF was prepared. The experimental procedure was as described before for compounds **4**, **5** and **6**. Yields: **12a** 71%, **12b** 55%, **13a** 49%, **13b** 69%, **13c** 43%, **20** 25%.

20: FTIR (KBr pellet) ν (cm^{-1}): 3078, 2942, 2874, 1740, 1641, 1606, 1580, 1513, 1471, 1423, 1393, 1318, 1242, 1167, 1063, 1009, 912, 846, 785, 763, 692, 653, 602, 550. MS (EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. intensity in %): 430 (15) [M], 203 (100), 121 (40), 55 (15), 41 (10). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.15 (d, 2H), 7.0 (m, 3H), 6.70 (m, 1H), 5.85 (m, 2H), 5.03 (m, 4H), 4.07 (m, 4H), 2.15 (m, 4H), 1.85 (m, 4H), 1.60 (m, 4H).

5.4.2. 4-[3-(Oxiran-2-yl)propoxy]-2,3-dicyanophenyl 4-[3-(oxiran-2-yl)propoxy]benzoate (14a), 4-[4-(oxiran-2-yl)butoxy]-2,3-dicyanophenyl 4-[4-(oxiran-2-yl)butoxy]benzoate (14b), 4-[(oxiran-2-yl)methoxy]phenyl 4-[(oxiran-2-yl)methoxy]benzoate (15a), 4-[2-(oxiran-2-yl)ethoxy]phenyl 4-[2-(oxiran-2-yl)ethoxy]benzoate (15b), 4-[4-(oxiran-2-yl)butoxy]phenyl 4-[4-(oxiran-2-yl)butoxy]benzoate (15c) and 4-[4-(oxiran-2-yl)butoxy]-2,3-difluorophenyl 4-[4-(oxiran-2-yl)butoxy]benzoate (21). To 20 ml 1,2-dichloroethane in a 100 ml flask equipped with mechanical stirrer, thermometer and reflux condenser, 2.25 mmol of the appropriate olefin (**12a**, **12b**, **13a–c** and **20**) and 0.03 mmol tetrakis(diperoxotungsto)phosphate [18, 19] was added. Then 10 ml 16% (24 mmol) H_2O_2 was introduced. The experimental procedure was as described before for compounds **7**, **8** and **9**. Yields: **14a** 94%, **14b** 48%, **15a** 49%, **15b** 69%, **15c** 43%, **21** 25%.

21: FTIR (KBr pellet) ν (cm^{-1}): 3055, 2948, 2853, 1733, 1602, 1511, 1500, 1474, 1397, 1320, 1260, 1243, 1164, 1066, 1009, 912, 854, 790, 766, 696, 604, 515. MS (EI, 70 eV, direct inlet 200°C) *m*/*z* (rel. intensity in %): 462 (20) [M], 219 (100), 121 (32), 99 (10), 81 (10), 57 (7), 43 (8). ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.10 (d, 2H), 7.07 (m, 4H), 4.17 (m, 4H), 2.83 (m, 2H), 2.66 (m, 2H), 2.42 (m, 2H), 2.05 (m, 4H), 1.87 (m, 4H), 1.63 (m, 4H).

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