The design and investigation of laterally functionalised oxadiazoles

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The synthesis of new [1,3,4]-oxadiazole-based mesogens with nematic phase behaviour at low temperature is described, and their characterisation by OPM, DSC and XRD is reported.

Introduction

Liquid crystals containing an oxadiazole group in the aromatic core have attracted considerable attention in recent years due to the observation of biaxial nematic phase behaviour in bent core materials.^{1–6} Additionally, the formation of chiral domains in smectic phases of non-chiral compounds, is of both experimental and theoretical interest.^{7–9}

The investigation of this class of materials is therefore important for the fundamental understanding of structure– properties relationships of mesomorphic systems. Investigations are, however, very often hampered by the generally high transition temperatures observed for oxadiazoles, where the nematic phase occurs mostly at temperatures well above $150 \,^{\circ}C.^{1,96,10}$ High transition temperatures in organic materials make investigations more difficult and there is the concern about long term stability of the materials in the liquid-crystal phase. This is the impetus to prepare materials that show mesomorphic phase behaviour below 100 °C, where there is usually less worry about the stability of organic liquid crystals and where physical measurements can be carried out more easily.

Informed by earlier work on laterally functionalised liquid crystals, such as polymers, dendrimers and organic– inorganic hybrids where wide mesomorphic phase ranges can be found and where depending on the scaffold selected, the occurrence of nematic, biaxial nematic, smectic C and columnar phase behaviour has been reported, it was decided that lateral functionalisation of the oxadiazole core could be a promising route towards new mesomorphic oxadiazole derivatives with liquid-crystal behaviour at low temperatures.^{11–14}

The target molecules are shown in Scheme 1. The mesogens consist either of four or five aromatic rings and are flanked at the termini of the molecular long axes with alkyl chains of eight and eleven methylene groups. The asymmetric derivatives of [1,3,4]-oxadiazole were obtained by attaching different mesogenic units to the oxadiazole core in two stages, either by an etherification reaction (2) or an esterification reaction (5) (Scheme 1).

Experimental

Materials

All materials were used as purchased unless mentioned otherwise. All reactions involving DCC and DMAP were performed under a dry atmosphere of nitrogen. Silica gel 60 (Merck) was used for column chromatography. TLC was performed on silica gel plates (Merck, Silica gel F_{254}).

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-ECP 400 M Hz FT-NMR spectrometer. Chemical shifts are reported in ppm relative to TMS. Elemental analysis was performed on Fisons EA1108 CHN. Thermal properties were investigated using a Mettler Toledo differential calorimeter (DSC 822^e) in nitrogen against an indium standard. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm. The mesophases were studied on an Olympus BH-2 optical polarising microscope, equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software Studio Capture, supplied by Studio 86 Designs was used for image capturing. XRD studies were performed on a MAR345 diffractometer, equipped with 2D detector, CuKa radiation source, graphite monochromator, $\lambda = 1.541$ Å. FIT2D and Origin software packages were used for XRD data analysis.

General method of esterification

A mixture of 1 equiv. of phenol, 1.2 equiv. of acid, and 1.2 equiv. of DMAP dissolved in dry DCM was stirred for a couple of minutes and 1.2 equiv. of DIPC dissolved in dry dichloromethane is added dropwise. The reaction mixture was left stirring for 12–24 h at room temperature in an inert atmosphere of nitrogen. After removal of the DIPU by-product by filtration, the solvent was concentrated and the product was purified by column chromatography on silica with the appropriate mixture of solvents.

2-(4-Undecyloxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4]-oxadiazole (2)

1 (1.6 g, 6.28 mmol), 40 ml dry DMF, K_2CO_3 (1.6 g, 12.56 mmol), KI (0.52 g, 3.14 mmol), undecyl bromide (1.01 g, 4.3 mmol) (dissolved in 20 ml dry DMF), 80 °C, 10 h,

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a) C₁₁H₂₃Br, K₂CO₃, KI, DMF b) 4-Undecyloxy-benzoic acid, CH₂Cl₂, DMAP, DIPC, rt;
c) Karstedt catalyst, toluene, 1,1,1,3,3-pentamethyl-disiloxane;
d) i. 4-Octyloxy-2-pent-4-enyloxy-benzoic acid, SOCl₂ ii.DMF, DMAP.

Scheme 1 Synthesis of unsymmetrical [1,3,4]-oxadiazole derivatives.

purification by column chromatography on silica (hexaneethyl acetate, 1 : 1), red–orange product, yield 0.61 g (24%), ¹H NMR $\delta_{\rm H}$ (CDCl₃): 8.03 (d, 2H, Ar), 8.0 (d, 2H, Ar) 7.02 (d, 2H, Ar), 7.00 (d, 2H, Ar), 4.02 (t, 2H, –CH₂–O), 1.81 (quin, 2H, C–CH₂–C), 1.65 (m, 2H, aliphatic), 1.47–1.26 (m, 14H, aliphatic) 0.88 (t, 3H, –CH₃), ¹³C NMR $\delta_{\rm C}$ (CDCl₃): 164.30, 160.70, 128.79, 128.53, 117.0, 114.94, 68.25, 31.88, 30.92, 29.52, 25.9, 22.6, 14.0. Anal. Calcd for C₂₅H₃₂N₂O₃: C 73.5, H 7.90, N 6.86, found C 73.1, H 8.0 N 6.83.

2-{4-[4-Octyloxy-2-(pent-4-enyloxy)carbonyloxyphenyl]} phenyl-5-(4-undecyloxyphenyl)-[1,3,4]-oxadiazole (3)

Quantities: derivative **2** (0.11 g, 0.27 mmol), **3b** (0.09 g, 0.32 mmol), DIPC (0.037 g, 0.31 mmol), DMAP (catalytic), 30 ml dichloromethane, purification on silica (DCM containing 5% ethyl acetate), white product, yield 0.1 g (53%), mp 99 °C, ¹H NMR $\delta_{\rm H}$ (CDCl₃): 8.16 (d, 2H, Ar), 8.05 (dd, 3H, Ar), 7.37 (d, 2H, Ar), 7.01 (d, 2H, Ar), 6.51 (dd, 2H, Ar), 5.81 (m, 1H, -CH=), 4.98 (qq, 2H, =CH₂), 4.03 (m, 6H, -O-CH₂), 2.27 (qv, 2H, -CH₂-), 1.94 (q, 2H, -CH₂-), 1.81 (m, 4H, -CH₂-), 1.38 (m, 26H, -CH₂-), 0.88 (m, 6H, -CH₃). Anal. Calcd for C₄₅H₆₀N₂O₆: C 74.55, H 8.34, N 3.86; found C 74.50, H 8.36, N 3.84.

2-{4-[4-Octyloxy-2-(5-(1,1,3,3,3-penthamethyldisiloxanyl) penthyloxy)carbonyloxy]}phenyl-5-(4-undecyloxyphenyl)-[1,3,4]-oxadiazole (4)

To (1 equiv.) and 5 equiv. of 1,1,1,3,3-pentamethyldisiloxane dissolved in dried DCM, Karstedt catalyst was added dropwise and the mixture was stirred at room temperature for 12 h.

Quantities: derivative **3** (0.8 g, 1.1 mol), 1,1,1,3,3-pentamethyldisiloxane (1.63 g, 11.03 mmol), 20 drops of Karstedt catalyst, 40 ml DCM, purification on silica (DCM) and precipitation in hexane, mp 83 °C, white–yellowish product, yield 0.4 g (42%), ¹H NMR $\delta_{\rm H}$ (CDCl₃): 8.13 (d, 2H, Ar), 8.03 (d, 2H, Ar), 8.01 (d, 1H, Ar), 7.35 (d, 2H, Ar), 6.98 (d, 2H, Ar), 6.50 (dd, 2H, Ar), 4.00 (m, 6H, –O–CH₂–), 1.80 (m, 6H, –CH₂–), 1.32 (m, 30H, –CH₂–), 0.84 (m, 6H, –CH₃), 0.46 (m, 2H, –CH₂–Si), 0.00 (m, 15H, Si(CH₃)),¹³C NMR $\delta_{\rm C}$ (CDCl₃): 164.84, 163.53, 162.08, 161.99, 155.89, 153.93, 134.65, 128.79, 128.79, 128.21, 122.91, 122.91, 122.33, 116.21, 115.08, 110.66, 105.47, 100.24, 69.01, 68.48, 68.38, 32.00, 31.89, 29.70, 29.65, 29.47, 29.43, 29.32, 29.22, 28.93, 26.08, 23.10, 22.78, 22.75, 18.35, 14.20, 2.06, 0.40. Anal. Calcd for C₅₀H₇₆N₂O₇Si₂: C 68.76, H 8.77, N 3.21; found C 68.8, H 8.75, N 3.19.

2-[4-(4-undecyloxyphenylcarbonyloxy)phenyl]-5-(4-hydroxyphenyl)-[1,3,4]-oxadiazole (5)

Preparation of the acid chloride. 4-Undecyloxybenzoic acid (0.47 g, 1.6 mmol) and 30 ml SOCl₂ were refluxed for 2 h and then concentrated under vacuum. The acid chloride obtain was used without further purification. A mixture of derivative 1 (0.5 g, 1.96 mmol) and DMAP (0.2 g, 1.6 mmol), dissolved in 20 ml dry DMF, was stirred for 15 min, and the acid chloride dissolved in 15 ml DCM was added dropwise. The reaction mixture was left stirring for 14 h, and the reaction was concentrated and the product was purified on silica gel (ethyl acetate–heptane, 1 : 1), white product, yield 0.34 g (39.24%), mp 186 °C, ¹H NMR $\delta_{\rm H}$ (DMSO): 10.31 (br s, 1H, –OH), 8.15 (d, 2H, Ar), 8.05 (d, 2H, Ar), 7.93 (d, 2H Ar), 7.50 (d, 2H, Ar),

7.08 (d, 2H, Ar), 6.95 (d, 2H, Ar), 4.05 (t, 2H, $-O-CH_{2-}$), 1.71 (qv, 2H, $-CH_{2-}$), 1.28 (m, 16H, $-CH_{2-}$), 0.81 (t, 3H, $-CH_3$), ¹³C NMR δ_C (DMSO): 164.99, 164.43, 164.12, 163.50, 161.55, 153.97, 132.69, 129.26, 128.58, 123.48, 121.85, 121.19, 116.76, 115.40, 114.85, 68.82, 31.78, 29.57, 29.14, 15.93, 22.52, 14.37. Anal. Calcd for C₃₂H₃₆N₂O₅: C 72.7, H 6.86, N 5.30; found C 72.9, H 6.85, N 5.32.

2-{4-[4-Octyloxy-2-(pent-4-enyloxy)carbonyloxyphenyl}phenyl-5-[4-(4-undecyloxy)carbonyloxyphenyl]phenyl-[1,3,4]oxadiazole (6)

Quantities: derivative **5** (0.2 g, 0.3 mmol), 4-octyloxy-2-pent-4enyloxybenzoic acid (0.15 g, 0.4 mmol), DIPC (0.05 g, 0.4 mmol), DMAP (catalytic), 40 ml CH₂Cl₂, purification on silica (DCM containing 10% ethyl acetate), white product, yield 0.22 g (68.81%), ¹H NMR $\delta_{\rm H}$ (CDCl₃): 8.21 (d, 2H, Ar), 8.19 (d, 2H, Ar), 8.15 (d, 2H, Ar), 8.04 (d, 1H, Ar), 7.41 (d, 2H, Ar), 7.38 (d, 2H, Ar), 6.98 (d, 2H, Ar), 6.53 (dd, 2H, Ar), 5.82 (m, 1H, -CH=), 4.99 (m, 2H, =CH₂), 4.04 (m, 6H,-O-CH₂-), 2.28 (q, 2H, -CH₂-), 1.95 (qv, 2H, -CH₂-), 1.80 (m, 4H, -CH₂-), 1.33 (m, 26 H, -CH₂-), 0.88 (t, 6H, -CH₃). Anal. Calcd for C₅₂H₆₄N₂O₈: C 73.91, H 7.63, N 3.31; found C 73.90, H 7.65, N 3.3.

2-{4-[4-Octyloxy-2-(5-(1,1,3,3,3-pentamethyldisiloxanyl)pentyloxyphenylcarbonyloxy]}phenyl-5-[4-(4-undecyloxy)carbonyloxyphenyl]phenyl-[1,3,4]-oxadiazole (7)

A mixture of (1 equiv.) and 5 equiv. of 1,1,1,3,3-pentamethyldisiloxane was dissolved in dried DCM, Karstedt catalyst was added dropwise, and the mixture was stirred at room temperature for 12 h. Quantities: derivative 6 (0.05 g, 0.05 mmol), 1,1,1,3,3-pentamethyldisiloxane (0.08 g, 0.59 mmol), 15 drops of Karstedt catalyst, 35 ml DCM, purification on silica (DCM) and precipitation with hexane, white-yellowish product, yield 51 mg (88%), ¹H NMR $\delta_{\rm H}$ (CDCl₃): 8.18 (d, 2H, Ar), 8.16 (d, 2H, Ar), 8.14 (d, 2H, Ar), 8.11 (d, 2H, Ar), 8.01 (d, 1H, Ar), 7.38 (d, 2H, Ar), 7.36 (d, 2H, Ar), 6.95 (d, 2H, Ar), 6.50 (dd, 2H, Ar), 4.01 (q, 6H, -O-CH₂-), 1.79 (m, 6H, -CH₂-), 1.36 (m, 24H, -CH₂-), 0.85 (t, 6H, -CH₃), 0.46 (m, 2H, -CH₂-Si), 0.00 (m, 15H, $-CH_3$), ¹³C NMR δ_C (CDCl₃): 164.86, 164.55, 164.31, 164.14, 163.92, 163.50, 162.01, 154.14, 153.89, 134.66, 132.51, 128.43, 128.36, 122.98, 122.82, 121.46, 121.09, 121.04, 114.51, 110.62, 105.48, 100.24, 69.01, 68.48, 32.00, 31.90, 29.70, 29.68, 29.64, 29.45, 29.43, 29.32, 29.22, 29.17, 28.94, 26.07, 23.11, 22.78, 22.75, 18.36, 14.22. Anal. Calcd for C₆₈H₇₈N₂O₉Si₂: C 68.67, H 8.03, N 2.86; found C 68.7, H 7.98, N 2.9.

Results and discussion

The investigation of the liquid-crystal phase behaviour of the systems **3**, **4**, **6** and **7** showed that only materials **6** and **7** exhibit mesomorphic behaviour. **3** melts at 99.0 °C and **4** at 83.0 °C from the crystalline state to an isotropic liquid. The samples crystallise on cooling. Increasing the size of the mesogenic moiety by one aromatic group leads to compounds **6** and **7** (Fig. 1 and 2).

The aromatic core system, though tilted, due to the presence of the oxadiazole group is essentially symmetric, the symmetry



Fig. 1 Textures of 6 (top) and 7 (bottom) in the N-phase.

is reduced by the different lengths of the terminal alkyl chains, containing eight and eleven methylene groups and most importantly by the lateral alkyl chain (pentenyloxy group) in $\bf{6}$ and further by the attached pentamethyldisiloxane group in $\bf{7}$.

The transition temperatures and enthalpies are summarised in Table 1.

Compared to symmetrical oxadiazole derivatives^{1,9,10,15-17} as well as recently reported non-symmetrical systems,^{18,19} which do not contain lateral chains, the melting points of 6 and 7 are relatively low, with 108.3 °C for 6 and only 65.4 °C for 7, the siloxane group being responsible for the reduction of the melting point by about 43 °C. In other words, the effect of lateral substitution on the transition temperatures is significant. The materials do not show enantiotropic LC behaviour, but supercooling of the isotropic melt leads to the formation of a nematic phase at 104.3 °C for 6 and 63.1 °C for 7 with an onset for the crystallisation at 62.5 °C for 6 and 52.4 °C for 7, resulting in a nematic phase range of 41.8 °C for 6 and 10.7 °C for 7. The reduction of the stability of the nematic phase by about 40 °C by the attachment of pentamethylsiloxane to a short lateral chain, is in line with behaviour observed for laterally substituted linear mesogens where reductions between 30 to 50 °C have been detected when short siloxane groups have been attached.²⁰ Fig. 1 shows formation of the nematic textures for 6 and a fully formed Schlieren texture for 7, shown at the bottom of Fig. 1. The texture at the isotropic to nematic texture is grainier and the fully formed texture is more threadlike. Fig. 2 shows the DSC traces for 6 and 7. The transition enthalpies for the isotropic to nematic transition are rather low, at 0.8 J g^{-1} and 0.13 J g^{-1} , with the siloxane substituted system 7 exhibiting the lower value. This suggests a much smaller increase of ordering going from the isotropic to the nematic phase compared to system 6. However the enthalpy values are quite similar to related linear systems Typical nematic Schlieren textures can be observed for both systems and notable is the large number of 2-brush defects.



Fig. 2 DSC curves of derivatives: (a) 6 and (b) 7, for rates of $10 \,^{\circ}$ C min⁻¹. 3rd heating and cooling runs are shown.

Table 1 Phase transitions (°C) of the asymmetric [1,3,4]-oxadiazole mesogens, enthalpies of nematic to isotropic transitions $[J g^{-1}]$, ^{*a*}transition recorded on cooling

3	Cr 99.0 Iso
4	Cr 83.0 Iso
6 7	Cr 108.3 (62.5 ^{<i>a</i>} N 104.3 (0.80)) Iso Cr 65.4 (52.4 ^{<i>a</i>} N 63.1 (0.13)) Iso
^{<i>a</i>} Monotropic transitions	

The phase structure of materials **6** and **7** was investigated further by XRD investigations of samples in capillaries. Fig. 3, shows an X-ray diffractogram of **6** and **7** at 90 °C and 64 °C, and Fig. 3b shows the radially integrated pattern (representation similar to 1D powder pattern).

The diffraction patterns show typical features for low ordered liquid crystals, diffuse wide-angle intensities, associated with the intermolecular distances of the oriented mesogens at (q = 1.41) 4.45 Å and pseudo Bragg-type small-angle reflections for (q = 0.19) d = 33.05 Å. However, the occurrence of four off-meridonal small-angle reflections is unusual in the nematic phase and is typically observed for a



Fig. 3 Diffractograms and radially integrated patterns of compound 6 at T = 90 °C (top) and compound 7 at T = 64 °C (bottom) collected on cooling.

smectic C (SmC) phase. The relatively low intensity of these reflections, when compared to the values measured for the wide-angle intensities in conjunction with OPM and DSC data suggests the formation of cybotactic clusters in the nematic phase. It should be noted that small-angle reflections can also be the signature of biaxial nematic phase behaviour.³ However, as the samples in this investigation were only aligned uniaxially, the distinction between cybotactic nematic clustering and nematic biaxilaty is not possible. Azimuthal scans of the small angle reflections, examples are shown in Fig. 4 allow the identification of a tilt angle of approximately 45.5° in the cybotactic clusters, which might be attributed to the presence of short range smectic (SmC)-like layer fluctuations. A variation of the temperature between 95 and 90 °C leads to



Fig. 4 Azimuthally integrated pattern of compound **6** at T = 90 and 95 °C, recorded on cooling.

no significant change in the apparent tilt. Furthermore, the intensity of these small angle reflections does not change much with temperature change. The apparent tilt of 45.5° is higher than the tilt observed for non-symmetric oxadiazoles in the SmC phase,^{9b} however somewhat lower than the values observed for siloxane substituted laterally functionalised linear calamitics, where values between 50 to 60° for the apparent tilt have been observed for the cybotactic nematic clusters.^{14e} Radial scans through the intensity maxima of these small-angle peaks and fitting of the integrated intensities with a Lorenztian distribution functions allows the determination of the halfwidth at half maximum (HWHM) of these peaks. With the help of the Scherrer equation ($\xi = 2\pi (0.89/(q_0 - q_{\rm HWHM}))$) an estimation of the correlation length ξ of the clusters, a measure of the length of the short range positional ordering can be obtained.²¹⁻²³ For material **6** a value of 53 Å was determined, which is not much larger than the apparent spacing d = 33.05 Å in the cybotactic clusters. This is indicative of a very short range of this ordering and confirms the essentially nematic character of the material in the mesophase. The investigation of 7 proved to be more difficult as the sample tended to crystallise more easily on supercooling resulting in shorter times available for sample orientation and data collection. The value of (q = 0.207) d = 30.34 Å found for the small angle reflection of 7 and the corresponding correlation length ξ of 37 Å are slightly smaller than the values detected for 6. This is in line with the DSC data and supports the observation that increasing the size of the lateral substituent decreases the ordering and the stability of the mesophase.

Conclusions

The lateral functionalisation of oxadiazole-based bent core mesogens with alkyl chains and siloxane groups is a viable route to lower the melting points and transition temperatures for such materials below 100 $^{\circ}$ C. This approach can be used to arrive at materials with exclusively nematic liquid-crystal phase behaviour.

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