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Synthesis and mesomorphic properties of new liquid crystalline stilbene derivatives containing vinyloxyalkoxy chains

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New liquid crystalline stilbene derivatives containing vinyloxyalkoxy chains **1** ($n = 5, 7, 9, 11$) have been synthesised. Their mesomorphic properties have been studied by polarising optical microscopy and differential scanning calorimetry. It is interesting to note that even their alcohol precursors showed liquid crystalline behaviour. The effect of terminal alkoxy chain length and UV irradiation on the mesomorphic behaviour is discussed.

1. Introduction

The control of alignment in optically active polymers is important in both fundamental and applied research because of its applications in opto-electronics and electro-optics. The in-plane alignment of such polymers can be carried out by several techniques including electric field poling [1], mechanical action (shear, stretching, rubbing) [2], and photoalignment in photoisomerizable or photodimerizable compounds [3]. The later materials are interesting for their ability to 'respond' to a light beam command by changing their molecular conformation or aggregation.

A different technique by which to control the polymer alignment is their growth from aligned liquid crystalline monomers [4]. Indeed, the anisotropic properties of liquid crystals allow them to be easily aligned by an electric or magnetic field, by mechanical action, or by an alignment agent coated on the cell substrates (surfactants, lecithins, polyimides, etc.) [5]. If the polymerization of aligned monomers is subsequently initiated, a preferentially aligned polymer can be obtained. Thus, the development of new liquid crystalline molecules bearing a function able to undergo polymerization is an area of particular interest, owing to the possibility of carrying out polymerization reactions in the liquid crystalline phase. Even greater

interest is obtained if the monomers contain a photo-responsive chemical group.

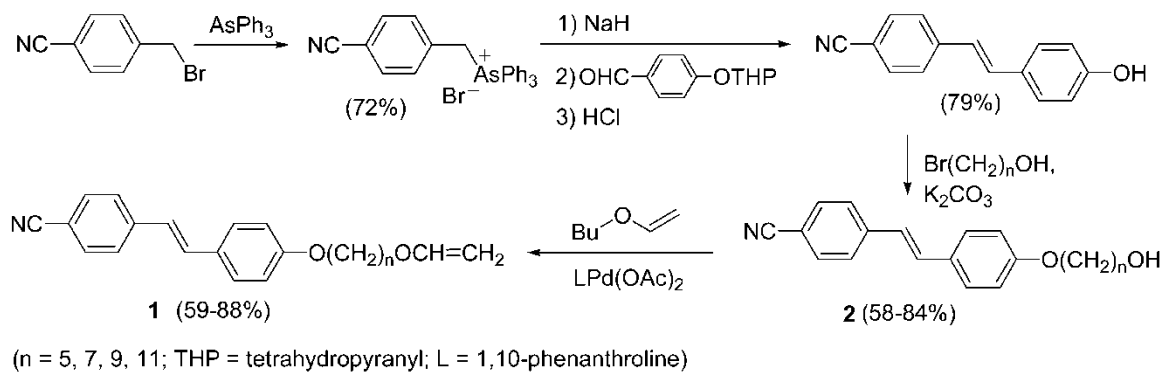
We report herein the synthesis and the study of the mesomorphic properties of new liquid crystalline stilbene derivatives **1** containing an aliphatic chain terminating with an enol ether function, suitable for cationic polymerization. During the synthesis, we observed that even their alcohol precursors **2** showed liquid crystalline behaviour, and we also report their transition temperatures and enthalpy changes.

2. Synthesis

The starting materials triphenylarsine, 4-cyanobenzyl bromide, 4-hydroxybenzaldehyde, 3,4-dihydro-2*H*-pyran, pentane-1,5-diol, heptane-1,7-diol, nonane-1,9-diol, 11-bromoundecan-1-ol were commercially available and used without further purification. 4-(Tetrahydropyran-2-yloxy)benzaldehyde, 5-bromopentan-1-ol, 7-bromoheptan-1-ol and 9-bromononan-1-ol were prepared according to literature procedures.

All the compounds **1** were synthesized according to the general route shown in the scheme, involving the following steps: (a) Wittig reaction between (4-cyanobenzyl)triphenylarsonium bromide and *O*-protected 4-hydroxybenzaldehyde, followed by deprotection to give 4-[2-(4-hydroxyphenyl)vinyl]benzonitrile; (b) Williamson reaction between the latter and the appropriate bromoalcohol; (c) palladium-catalysed exchange

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Scheme. Synthesis of compounds **1**.

reaction between the alcoholic group of the resulting products **2** and butyl vinyl ether. A description of the synthesis of compounds **1** is given.

2.1. (4-Cyanobenzyl)triphenylarsonium bromide [6]

A solution of triphenylarsine (10.1 g, 33.0 mmol) and 4-cyanobenzyl bromide (9.0 g, 45.9 mmol) in MeCN (50 ml) was allowed to stir at r.t. for 72 h. The solvent was removed by rotary evaporation to give crude (4-cyanobenzyl)triphenylarsonium bromide, which was recrystallized several times from CH₂Cl₂/Et₂O solutions to give a colourless solid, m.p. 186–187°C, literature [7] 188–189°C (total yield: 16.6 g, 72% based on 4-cyanobenzyl bromide, 100% based on triphenylarsine).

2.2. 4-[2-(4-Hydroxyphenyl)vinyl]benzonitrile

The method of Tewari and co-workers [8] was employed. (4-Cyanobenzyl)triphenylarsonium bromide (15.0 g, 29.9 mmol) was added under nitrogen to a stirred suspension of NaH (715 mg, 29.8 mmol) in anhydrous THF (190 ml). After additional stirring at r.t. for 0.5 h, 4-(tetrahydropyran-2-yloxy)benzaldehyde (6.1 g, 29.6 mmol) was added and the resulting mixture was allowed to stir at r.t. for 48 h. After acidification with 0.1N HCl (150 ml), CHCl₃ was added, phases were separated and the aqueous layer was extracted with CHCl₃. The collected organic phases were dried over CaCl₂, the solvent was eliminated by rotary evaporation and the residue dissolved in MeOH (130 ml). Conc. HCl (4.4 ml) was added, and the resulting mixture heated at reflux for 2 h. Saturated aqueous NaHCO₃ (100 ml) and Et₂O (100 ml) were then added to the cooled mixture, and the phases were separated. The aqueous layer was extracted three times with Et₂O, and the collected organic phases were dried over CaCl₂. Elimination of the solvent by rotary evaporation afforded crude 4-[2-(4-hydroxyphenyl)vinyl]benzonitrile, which

was crystallized several times from CHCl₃/Et₂O to give colourless crystals (5.24 g, 80%).

2.3. General procedure for the preparation of (E)-4-{2-[4-(ω-hydroxyalkyloxy)phenyl]vinyl}benzonitrile derivatives **2**

The appropriate ω-bromoalcohol Br(CH₂)_nOH (16.1 mmol) was added under nitrogen to a solution of 4-[2-(4-hydroxyphenyl)vinyl]benzonitrile (2.6 g, 11.8 mmol), K₂CO₃ (3.2 g, 23.2 mmol) and KI (2.5 g, 15.1 mmol) in anhydrous DMSO (60 ml). The mixture was heated with stirring at 110°C for 18 h. After cooling, water and CHCl₃ were added and phases separated. The organic layer was washed several times with water and dried over Na₂SO₄. After removal of the solvent by rotary evaporation, crude products were purified by column chromatography on silica gel using as eluant CHCl₃/acetone = 9/1 (n = 5, 72% yield based on 4-[2-(4-hydroxyphenyl)vinyl]benzonitrile); CH₂Cl₂/hexane from 9/1 to 10/0 (n = 7, 69%); CH₂Cl₂ (n = 9, 84%); CHCl₃/hexane from 9/1 to 10/0 (n = 11, 91%).

2.4. General procedure for the preparation of 4-{2-[4-(5-vinyloxy)pentyl]phenyl}vinyl benzonitrile derivatives **1**

The method of Percec *et al.* [9] was employed. The appropriate derivative **2** (1.28 mmol) was added to a solution of (1,10-phenanthroline)palladium(II) diacetate (51.5 mg, 0.13 mmol) in butoxyethene (6.8 ml) and CHCl₃ (1.6 ml). The mixture was heated with stirring at 60°C for 6 h. After cooling, the mixture was filtered and solvent removed from the filtrate by rotary evaporation. Crude products were purified by column chromatography on silica gel using as eluant CHCl₃/hexane = 8/2 (n = 5, 79% yield); CHCl₃/hexane = 8/2 (n = 7, 68%); CH₂Cl₂/hexane = 9/1 (n = 9, 59%); CHCl₃/hexane = 7/3 (n = 11, 88%).

2.5. Chemical characterization of representative products

All products were fully characterized by spectroscopic techniques and elemental analysis. Here we report representative data for compounds **1** and **2** with $n=7$.

2.5.1. (E)-4-[2-(4-Hydroxyphenyl)vinyl]benzonitrile

Colourless solid, m.p. 221–222. IR (KBr) 3311 (m, br), 2237 (m), 1597 (m), 1583 (m), 1514 (m), 1173 (m), 837 (s) cm^{-1} . ^1H NMR (acetone- d_6) δ 7.86–7.62 (m, 4 H aromatic), 7.73 (s, 1 H, OH), 7.54–7.48 (m, 2 H aromatic), 7.38 (distorted d, $J=16.6$, 1 H, =CH), 7.12 (distorted d, $J=16.6$, 1 H, =CH), 6.93–6.86 (m, 2 H aromatic), ^{13}C NMR (acetone- d_6) δ 159.1, 143.6, 133.2, 132.3, 130.7, 129.4, 127.5, 124.5, 119.6, 116.6, 110.6. Anal: calcd for $\text{C}_{15}\text{H}_{11}\text{NO}$, C 81.43, H 5.01, N 6.33; found, C 81.52, H 5.03, N 6.35%.

2.5.2. (E)-4-{2-[4-(7-Vinyloxyheptyloxy)phenyl]vinyl}benzonitrile **1** ($n=7$)

Colourless solid. IR (KBr) 2941 (m), 2866 (m), 2219 (m), 1597 (s), 1513 (m), 1251 (s), 831 (s), 556 (m) cm^{-1} . ^1H NMR (CDCl_3) δ 7.63–7.58 (m, 2 H aromatic), 7.56–7.51 (m, 2 H aromatic), 7.49–7.43 (m, 2 H aromatic), 7.16 (distorted d, $J=16.6$, 1 H, =CH), 6.94 (distorted d, $J=16.6$, 1 H, =CH), 6.93–6.87 (m, 2 H aromatic), 6.47 (dd, $J=14.2$, 6.8, 1 H, OCH=), 4.17 (dd, $J=14.2$, 2.0, 1 H, =CHH), 4.02–3.95 (m, 3 H, =CHH+OCH $_2$), 3.68 (t, $J=6.8$, 2 H, OCH $_2$), 1.86–1.75 (m, 2 H, CH $_2$), 1.73–1.63 (m, 2 H, CH $_2$), 1.55–1.33 (m, 6 H, 3 CH $_2$). ^{13}C NMR (CDCl_3) δ 159.7, 152.0, 142.3, 132.5, 132.0, 128.9, 128.3, 126.5, 124.4, 119.1, 114.9, 110.0, 86.3, 68.0, 29.2, 29.1, 29.0, 26.0. Anal: calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_2$, C 79.74, H 7.53, N 3.87; found, C 79.83, H 7.55, N 3.85%.

2.5.3. (E)-4-{2-[4-(5-Hydroxyheptyloxy)phenyl]vinyl}benzonitrile **2** ($n=7$)

Colourless solid. IR (KBr) 3329 (w, br), 2936 (m), 2857 (m), 2225 (w), 1598 (m), 1513 (m), 1261 (s), 1180 (m), 1055 (m), 971 (w), 835 (s), 555 (m) cm^{-1} . ^1H NMR

(CDCl_3) δ 7.63–7.57 (m, 2 H aromatic), 7.56–7.50 (m, 2 H aromatic), 7.48–7.42 (m, 2 H aromatic), 7.15 (distorted d, $J=16.6$, 1 H, =CH), 6.93 (distorted d, $J=16.6$, 1 H, =CH), 6.93–6.86 (m, 2 H aromatic), 3.97 (t, $J=6.3$, 2 H, OCH $_2$), 3.65 (t, $J=6.6$, 2 H, OCH $_2$), 1.85–1.74 (m, 2 H, CH $_2$), 1.64–1.32 (m, 8 H, 4 CH $_2$). ^{13}C NMR (CDCl_3) δ 159.6, 142.3, 132.4, 132.0, 128.9, 128.3, 126.5, 124.4, 119.2, 114.8, 109.9, 68.0, 62.9, 32.7, 29.2, 26.0, 25.7. Anal: calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_2$, C 78.77, H 7.51, N 4.18; found, C 78.92, H 7.49, N 4.20%.

3. Characterization

Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba Elemental Analyser Mod. 1106. ^1H NMR and ^{13}C NMR spectra were taken on a Bruker AC300 spectrometer and run in CDCl_3 solutions with Me_4Si as internal standard and recorded at 300 MHz and 75 MHz, respectively. Chemical shifts and coupling constants (J) are given in ppm (δ) and in Hz, respectively. IR spectra were taken on a Perkin-Elmer Paragon 1000 PC FTIR spectrometer. All reactions were analysed by TLC on silica gel 60 F $_{254}$, or by GLC using a Shimadzu GC-14A gas chromatograph and capillary columns with polymethylsilicone +5% phenylsilicone as the stationary phase (HP-5). Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh).

Transition temperatures and phase assignments were determined with a Leitz Laborlux 12 POL polarizing optical microscope in conjunction with a Linkam TH600 hot stage. The observed textures were compared with those reported in the literature [12]. The enthalpies of transitions were measured by differential scanning calorimetry using a Netzsch 2000-T4 calorimeter with a heating rate of $10^\circ\text{C min}^{-1}$.

An evaluation of the homogeneous alignment of compounds **1** was performed by filling into glass cells ($5\ \mu\text{m}$ thick, anti-parallel polyimides coating, Linkam) in their nematic state and measuring the transmittance

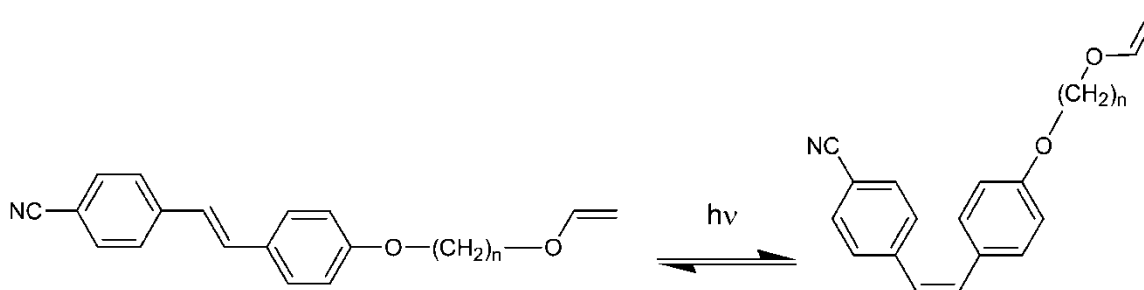


Figure 1. *Trans*- and *cis*-forms of compounds **1**.

Table 1. Transition temperatures and enthalpy changes for compounds **1**. Cr=crystal; Sm A=smectic A phase; N=nematic phase; I=isotropic phase.

<i>n</i>	Transition temperatures/ $^{\circ}\text{C}$ and enthalpy changes (kJ mol^{-1})
5	Cr 70.4 (7.1) SmA 74.0 (8.5) N 74.7 (10.3) I
7	Cr 61.5 (5.3) SmA 71.9 (16.3) N 78.1 (8.5) I
9	Cr 85.4 (11.1) N 87.9 (11.2) I
11	Cr 77.5 (2.2) N 96.3 (21.8) I

of the polarized probing He-Ne beam as a function of the rotational angle ϕ for the cross configuration of the polarizer and analyser. Photoisomerization of compounds **1** (see figure 1) was monitored by UV-vis absorption spectroscopy with a Yasco 550 V UV-vis spectrometer as a function of energy supplied at 340 nm by a 200 W high pressure mercury lamp.

4. Results and discussion

The transition temperatures and enthalpy changes of compounds **1** are reported in table 1. All compounds **1** exhibit a nematic phase; compounds with a short alkoxy chain length ($n=5$, $n=7$) also show a smectic A phase. By contrast, the longer alkoxy chains tend to destabilize the smectic phase because of increased chain mobility.

It is important to note that even precursors **2** show liquid crystalline behaviour. The transition temperatures and enthalpy changes of compounds **2** are reported in table 2. Compounds **2** also show both nematic and smectic A phases with a trend similar to that shown by series **1**.

The evaluation of the homogeneous alignment of **1** gave a repeating pattern of valleys and peaks with a typical separation of 90° (see figure 2). This confirms that the cells are homogeneously well aligned. It is known that stilbenes show appreciable absorption in the solar spectral region. UV spectra and changes induced by the indicated periods of irradiation at 340 nm are shown in figure 3 for $n=7$. Before illumination all samples consisted of only the *trans*-form of the stilbene, because this isomer is

Table 2. Transition temperatures and enthalpy changes for compounds **2**. Cr=crystal; Sm A=smectic A phase; N=nematic phase; I=isotropic phase.

<i>n</i>	Transition temperatures/ $^{\circ}\text{C}$ and enthalpy changes (kJ mol^{-1})
5	Cr 88.8 (12.4) SmA 94.9 (16.3) N 104.8 (5.4) I
7	Cr 83.4 (15.6) N 91.3 (9.6) I
9	Cr 91.0 (28.8) N 98.4 (12.0) I
11	Cr 98.2 (14.2) N 101.2 (26.4) I

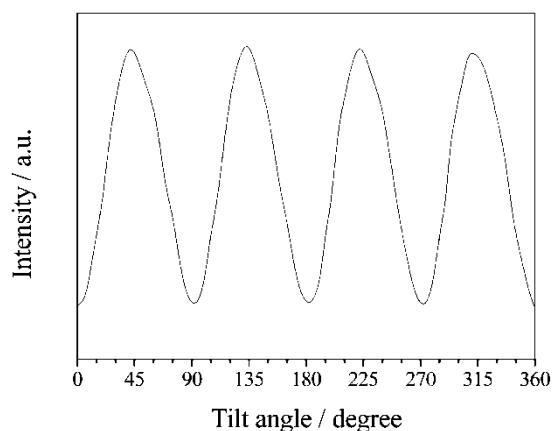


Figure 2. Transmittance through a homogeneous aligned cell of compound **1** ($n=7$) as a function of the rotational angle ϕ for the cross configuration of the polarizer and analyser.

thermodynamically more stable than the *cis*-form. Upon illumination with UV light, all compounds **1** clearly undergo a phototransformation of the *trans*-isomer to the *cis*-isomer in an almost complete manner. The phototransformation is manifest by the decreasing intensities of $\pi \rightarrow \pi^*$ absorptions at 340 nm. No thermal back reaction to *trans*-isomers was found, in agreement with the literature [13]. A relaxation back to the *trans*-form can be induced by irradiating cells with a 280 nm light beam for a few minutes. No photoinduced oligomerization or polymerization occurred in the samples, as confirmed by optical microscopy observations and by constant transition temperatures. This observation is in agreement with the chemical reactivity of the vinyl-ether moieties, which are known to polymerize only by a cationic initiator and not by a

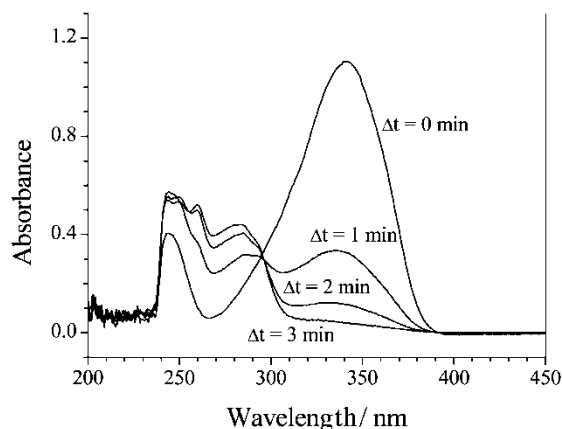


Figure 3. Changes in the UV spectra for compound **1** ($n=7$) induced by irradiation at 340 nm for different time intervals.

radical initiator. The photoisomerization was also confirmed by photoirradiation of aligned thin cells. In fact, if a UV beam impinged on a homogeneously aligned sample (in its nematic phase), we observed a phase transition to an isotropic state, because the *cis*-conformer is no longer liquid crystalline. This confirms the potential use of stilbene molecules as information processing and data storage materials.

5. Conclusions

We have synthesized and studied the properties of four new liquid crystalline stilbene derivatives containing vinyloxyalkoxy chains. Such compounds show both nematic and smectic A phases. They align in thin cells and upon irradiation with UV light lose their mesomorphic properties. The importance of this investigation is that the development of new liquid crystalline monomers bearing a photoresponsive chemical bond could allow the formation of an aligned polymer for interesting opto-electronic applications. Further investigation is now in progress on the chemical/physical properties of polymer films.

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